Hydrodechlorination of Trichloromethane to Higher Hydrocarbons over Pd/SiO_2 Catalyst

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Pd/SiO_2 catalyzed C–C bond formation selectively to give C_2–C_7 hydrocarbons in the hydrodechlorination of $CHCl_3$. The produced hydrocarbons followed well the Schultz–Flory distribution, indicating that the hydrocarbons were formed via polymerization of surface C_1 species such as methylene group.

Catalytic hydrodechlorination of chlorine-containing compounds has been studied extensively in recent years to convert them into environmentally benign and more useful products.[1–6] It has been known that C–C bond formation takes place during the hydrodechlorination of some compounds.[2–6] Over Ru/SiO_2, CCl_2F–$CClF_2$ is dehydrodechlorinated into $CClF{=}CF_2$[2] while CCl_3–CF_3 is dehydrodechlorinatively dimerized to form C_4 selectively (90% selectivity).[3] The hydrodechlorination of CCl_4 over Pd/C and Pd/TiO_2 yields hydrocarbons having chain length up to C_5[4] and that of CH_2Cl_2 over Pd/Al_2O_3 yields Cl–H replacement products, CH_4 and CH_3Cl, selectively.[7] Discrepancy is found in the reports on the hydrodechlorination of CCl_2F_2 over Pd/C. Wiersma et al.[5] have reported the selective Cl–H replacement to CH_2F_2 and Kulkarni et al.[6] do the oligomerization to give $CH_2{=}CF_2$, $CH_2{=}CH_2$, and C_3, although their reaction conditions are not very different. Recently, we found selective formation of hydrocarbons in the hydrodechlorination of $CHCl_3$ over silica-supported Pd catalysts. The results are reported here.

Various silica-supported noble metal catalysts were prepared by an ion-exchange method with an ammoniacal solution of $[Ru(NH_3)_6]Cl_3$, $[Rh(NH_3)_6]Cl_3$, $[Pd(NH_3)_4]Cl_2$, or $[Pt(NH_3)_4]Cl_2$. After allowing to ion-exchange for one day, the solids were filtered, dried in an oven overnight at 110 °C. Prior to the reaction catalyst was treated in a H_2 stream at 450 °C for 2 h. $CHCl_3$ (Kanto Chemical) was washed with distilled water to remove ethanol added as stabilizer and then dried with $CaCl_2$.

The reaction of $CHCl_3$ with hydrogen was carried out in a conventional flow-type reaction system with a Pyrex glass reactor under atmospheric pressure. The reaction conditions were as follows: temperature, 200 °C; feed composition (molar ratio), Ar : H_2 : $CHCl_3$ = 19.5 : 9.5 : 1; total flow rate, 60 cm^3 min^{-1}; catalyst amount, 0.100 g. The feed and effluent gases were analyzed by a gas chromatograph (Shimadzu GC-9A) equipped with a thermal conductivity detector and a flame ionization detector using a Gaskuropack 54 column (GL Sciences). The products were identified with a GC–MS (Hitachi M-80B) using the same column.

The results of hydrodechlorination of $CHCl_3$ over silica-supported noble metal catalysts are shown in Table 1, where the data obtained at 3 h on stream were summarized. Among the catalysts employed, Pd/SiO_2 was most active and the activity did not change appreciably with time on stream (92.2% conversion at 6 h on stream). The products were C_1–C_7 hydrocarbons for the most part and the Cl–H replacement product, CH_2Cl_2, was formed at the selectivity as low as 0.05%. The hydrocarbons produced were alkanes and the ratio of branched to normal for C_4, C_5, C_6, and C_7 was 0.16, 0.70, 0.97, and 1.3, respectively. Pt/SiO_2 also showed high activity for the reaction giving Cl–H replacement products, CH_4 and CH_2Cl_2, mainly but the activity decreased with time on stream gradually (77.4% conversion at 6 h on stream). Over Rh/SiO_2, hydrocarbons are formed at relatively high selectivity but the value of conversion was much lower than that over Pd/SiO_2 and decreased to 2.1% at 6 h on stream. Ru/SiO_2 catalyzed the dimerization of CCl_3–CF_3 reported previously,[3] but the catalytic activity for this reaction was very poor. Over Rh and Ru catalysts, the total selectivity of gaseous products was considerably low suggesting carbon deposition on the catalyst surface, and more than half of C_{2+} hydrocarbons produced were alkenes. Chlorine coverage on the metal surface under hydrodechlorination conditions increases in the order of Pd < Rh < Ru;[5,6] that is, the coverage of dissociatively adsobed hydrogen might decrease in the same order. It seems that insufficiency of adsorbed hydrogen on Rh and Ru causes the conversion of adsorbed C_1 species into alkenes and carbonaceous.

Table 1. Hydrodechlorination of trichloromethane over silica-supported noble metal catalysts at 200 °C

	Catalyst[a]			
	Pd (0.50)	Pt (0.92)	Rh (0.48)	Ru (0.47)
Conversion / %	93.9	89.9	6.5	1.4
Selectivity / %				
CH_2Cl_2	0.5	28.8	13.5	9.6
Hydrocarbon				
C_1	51.7	71.1	25.6	1.9
C_2	31.1	tr.	3.3	0.6
C_3	10.2	-	4.0	0.6
C_4	4.4	-	2.7	tr.
C_5	1.4	-	2.0	-
C_6	0.5	-	0.9	-
C_7	0.2	-	1.0	-

[a]The number in the parenthesis indicates the amount of metal loading (wt%) which corresponds to 47 μmol g-cat.$^{-1}$ for all catalysts.

Figure 1 presents the effect of reaction temperature on the hydrodechlorination of $CHCl_3$ over Pd/SiO_2. The values of conversion and selectivity were obtained after the reaction reached its steady state at each temperature. When the reaction temperature increased from 100 °C to 225 °C, the conversion of $CHCl_3$ increased from 1.85% to 98.8% and the Cl–H replaced product CH_2Cl_2 was always formed as minor products decreasing its selectivity from 1.7 to 0.5%. The selectivity for CH_4 decreased and those for C_{2+} alkanes increased with reaction temperature. In a supplemental study, the contact time did not give much influence to the product distribution. The result indicates that the carbon chain-growth reaction does not result

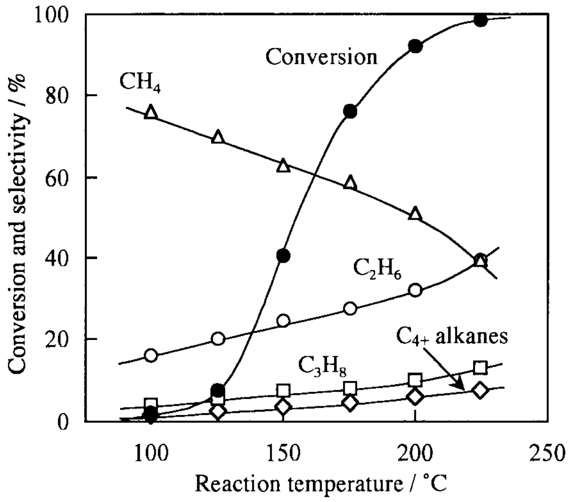

Figure 1. Hydrodechlorination of trichloromethane over 0.50 wt% Pd/SiO_2 at various temperatures.

from the consecutive C–C bond formation through the readsorption of desorbed molecules.

Figure 2 shows the Schultz–Flory plots for compositions of hydrocarbons formed over Pd/SiO_2 at various temperatures. The Schultz–Flory distribution is expressed by eq (1); where C_n is the mole fraction of the hydrocarbon with n_c carbon atoms and α represents the probability of chain-growth.[8]

$$\ln(C_n) = n_c \ln\alpha + \ln(C_1/\alpha) \qquad (1)$$

As seen in Figure 2, the composition of hydrocarbons formed at every temperature followed eq (1) at the correlation coefficient more than 0.994. This means that higher hydrocarbons are formed through the polymerization of surface C_1 species like a Fischer–Tropsh reaction. The probability of chain-growth (α) calculated from the slope of each line in Figure 2, was increased from 0.15 (100 °C) to 0.28 (200 °C) with reaction temperature. 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 (CH_2=) formed by dechlorination/hydrogenation of adsorbed $CHCl_3$, because the chlorine containing C_{2+} hydrocarbon is not detected in the products.

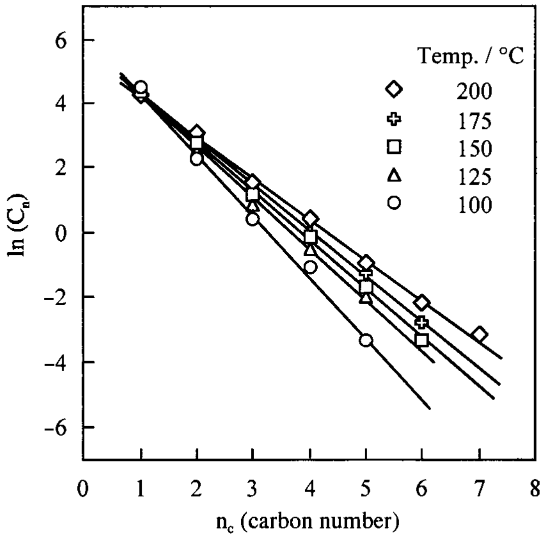

Figure 2. Shultz-Flory plots for hydrocarbons formed in the hydrodechlorination of trichloromethane over 0.50 wt% Pd/SiO_2.

C_{2+} hydrocarbons were not produced in the hydrodechlorination of CH_2Cl_2 and those including alkenes were formed in the reaction of CCl_4 over Pd catalysts. The difference of selectivity to oligomerization products is explainable by the reactivity of chloromethanes. The reactivity namely the tendency to C–Cl bond cleavage increases remarkably with the number of chlorine atoms in it ($CH_2Cl_2 < CHCl_3 < CCl_4$).[9] It is likely that CH_2Cl_2 adsorbs dissociatively on Pd at the lower coverage because of its lower reactivity, leading to the higher coverage of adsorbed hydrogen, and the surface C_1 species are attacked by adsorbed hydrogen preferentially to form Cl–H replacement products, CH_4 and CH_3Cl. The high reactivity of CCl_4 seems to cause the higher coverage of C_1 species and chlorine, resulting in the coupling into alkenes and marked deactivation by carbon deposit because of the shortage of adsorbed hydrogen.

The selective hydrocarbon formation from $CHCl_3$ we report here is expected to be a potential process for a methane conversion into hydrocarbons under mild condition, since CH_4 is converted easily to $CHCl_3$ by the reaction with Cl_2 and HCl formed can be oxidized back to Cl_2.

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