Direct synthesis of phenylchlorogermanes from metallic germanium and chlorobenzene using metal chloride catalysts

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In the direct synthesis of phenylchlorogermanes, copper(I) chloride was the best catalyst among the metal chlorides tested, the products being diphenyldichlorogermane and phenyltrichlorogermane. The reaction mainly gave diphenyldichlorogermane; however at the beginning of the reaction, phenyltrichlorogermane was afforded by the reaction of chlorobenzene and dichlorogermylene formed from metallic germanium and chloride ion in the catalyst.

KEY WORDS: direct synthesis; phenylchlorogermane; copper catalyst; silver catalyst; metallic germanium

1. Introduction

Methylchlorogermanes can be synthesized by the reaction of metallic germanium with methyl chloride using a copper catalyst [1–4]. This is called "direct synthesis," which is a very useful method for obtaining organogermanes [4]. During the reaction, the copper catalyst exists as a copper–germanium intermetallic compound [2], which forms an active area to afford methylchlorogermanes.

Rochow has reported the direct synthesis of phenylchlorogermanes from metallic germanium and chlorobenzene (equation (1)) [1], and has used a germanium–silver composite prepared by sintering germanium powder and silver powder as a catalyst. Copper(II) oxide has also been reported to catalyze the reaction of germanium with chlorobenzene; however the yield of the main product, phenyltrichlorogermane, was very low, 0.6% [5]. Copper(I) chloride is suitable for formation of copper–germanium alloy, because copper(I) chloride easily reacts with germanium to form the alloy on the germanium surface together with tetrachlorogermane (equation (2)) [6]. Therefore, metal chloride such as copper(I) chloride is expected as an active catalyst for the direct synthesis of phenylchlorogermanes. The aim of this work is finding an active metal chloride catalyst. In this work, silver(I), copper(II) or copper(I) chloride was tested as a catalyst, and the reaction pathways were examined:

$$\mathrm{Ge} + \mathrm{C_6H_5Cl} \rightarrow (\mathrm{C_6H_5})_n\mathrm{GeCl}_{4-n} \quad (n = 1\text{–}3) \qquad (1)$$

$$\mathrm{Ge} + 4\mathrm{CuCl} \rightarrow \mathrm{GeCl_4} + \mathrm{Cu\text{–}Ge\ alloy} \qquad (2)$$

2. Experimental

Germanium grains ($<45\ \mu$m) were treated with an aqueous hydrogen fluoride solution (46%) to remove native oxide overlayers, washed with a deionized water and dried. In a 120 ml autoclave, 6.9 mmol of the germanium grains, copper(I) chloride grains ($\mathrm{Cu/(Ge + CuCl)} = 20$ wt%) and 200 mmol of chlorobenzene were put. The autoclave was heated at 350 °C with stirring of the reaction mixture. After the reaction, the mixture was filtered, and the liquid obtained was analyzed by a gas chromatograph. The products were identified by GC-MS.

3. Results and discussion

3.1. Direct synthesis of phenylchlorogermanes using various metal chloride catalysts

The reaction of metallic germanium and chlorobenzene was carried out using 20 wt% of copper(I) chloride as a catalyst at 350 °C. Phenyltrichlorogermane, diphenyldichlorogermane and triphenylchlorogermane were formed as germanium-containing products. The time courses of the germanium conversion and the yields of the phenylchlorogermanes are shown in figure 1. At the beginning of the reaction, the main product was phenyltrichlorogermane, and finally the yields of diphenyldichlorogermane and phenyltrichlorogermane became almost the same. The amount of triphenylchlorogermane formed was very small. At 60 h, the germanium conversion reached 76%.

Instead of copper(I) chloride, copper(II) chloride was used as a catalyst. Figure 2 shows the time course of the reaction. Between 0 and 2 h of reaction time, only phenyltrichlorogermane was formed, while the amounts of phenyltrichlorogermane and diphenyldichlorogermane formed after 2 h were almost same. The germanium conversion was 62% at the end of the reaction, the selectivities for phenyltrichlorogermane and diphenyldichlorogermane being 65 and 35%, respectively.

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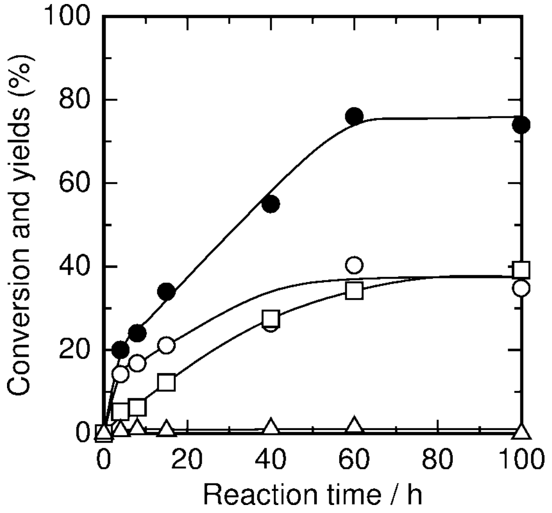


Figure 1. Time courses of the germanium conversion (•) and the yields of phenyltrichlorogermane (◦), diphenyldichlorogermane (□) and triphenylchlorogermane (△) using copper(I) chloride. Germanium grains (6.9 mmol), copper(I) chloride grains (20 wt%, 2.3 mmol) and chlorobenzene (200 mmol) were charged in an autoclave, and heated at 350 °C.

Silver(I) chloride also catalyzed the reaction. As shown in figure 3, a substantial induction period was observed. The yields of phenyltrichlorogermane and diphenyldichlorogermane rapidly increased around 10 h. The final germanium conversion, 43%, at 60 h was lower than those using the copper catalysts, and phenyltrichlorogermane was mainly formed with a 32% yield.

The copper chloride catalysts used gave germanium conversions over 60%, in contrast to the very low yield of phenyltrichlorogermane, 0.6%, reported using copper(I) oxide [6]. This indicates that copper chlorides, especially copper(I) chloride, are good catalysts for the direct synthesis of phenylchlorogermanes.

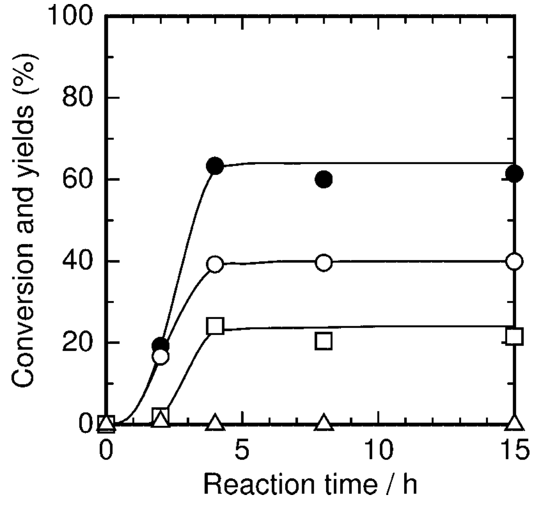


Figure 2. Time courses of the germanium conversion (•) and the yields of phenyltrichlorogermane (◦), diphenyldichlorogermane (□) and triphenylchlorogermane (△) using copper(II) chloride. Germanium grains (6.9 mmol), copper(II) chloride grains (20 wt%, 2.7 mmol) and chlorobenzene (200 mmol) were charged in an autoclave, and heated at 350 °C.

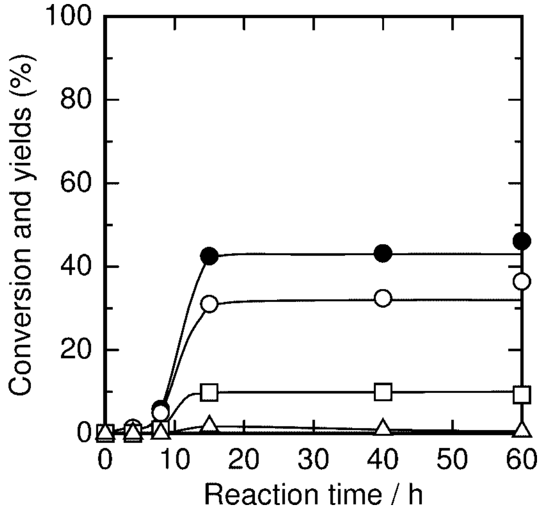


Figure 3. Time courses of the germanium conversion (•) and the yields of phenyltrichlorogermane (◦), diphenyldichlorogermane (□) and triphenylchlorogermane (△) using silver(I) chloride. Germanium grains (6.9 mmol), silver(I) chloride grains (20 wt%, 1.3 mmol) and chlorobenzene (200 mmol) were charged in an autoclave, and heated at 350 °C.

3.2. Effect of the amount of copper(I) chloride catalyst

The amount of copper(I) chloride was changed from 10 to 30 wt%. Using 30 wt% of the catalyst, the germanium conversion quickly increased to 52% at 15 h and the reaction almost stopped. When 20 wt% of the catalyst was used, the conversion increased rapidly to 4 h, and then gradually increased. After 40 h, the germanium conversion was higher than that using 30 wt%. Further decrease of the catalyst amount to 10 wt% decreased the consumption rate of metallic germanium.

Using 30 wt% of copper(I) chloride, the germanium conversion was 56% at 60 h, while the use of 20 wt% of the catalyst resulted in a conversion over 70%. Probably a larger

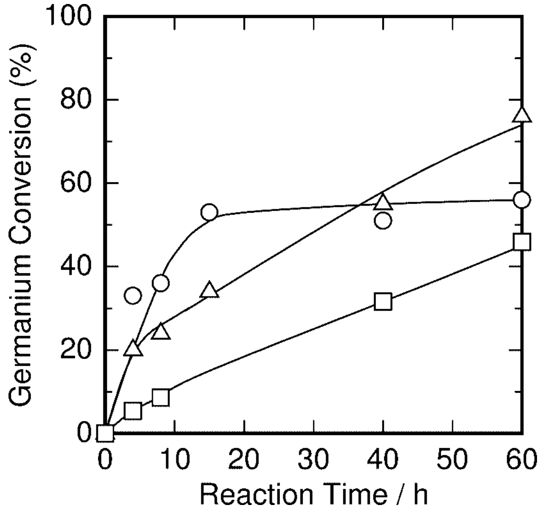


Figure 4. Time courses of the germanium conversion using 10 (□), 20 (△) and 30 wt% (◦) of copper(I) chloride. Germanium grains (6.9 mmol) and chlorobenzene (200 mmol) were charged in an autoclave, and heated at 350 °C.

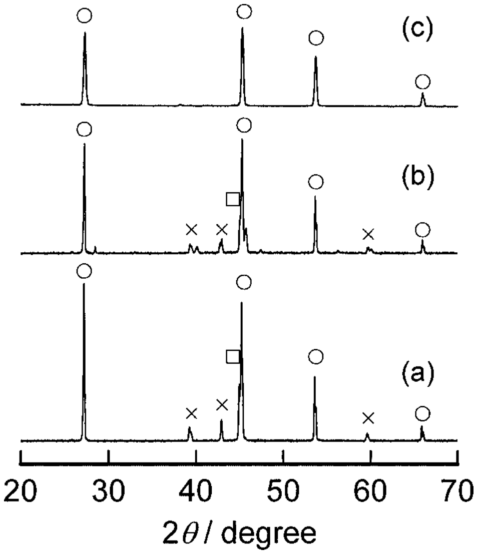
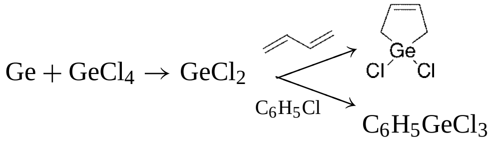


Figure 5. X-ray diffraction patterns of the mixture of metallic germanium (6.9 mmol) and the catalyst (20 wt%) after the reaction of germanium with chlorobenzene (200 mmol) at 350 °C. (a) Use of copper(I) chloride after 4 h reaction; (b) use of copper(II) chloride after 2 h reaction; (c) use of silver(I) chloride after 15 h reaction. (○) Germanium metal, (×) Cu_3Ge, and (□) metallic copper.

amount of copper more easily aggregates together to form a large copper metal whose formation leads to deactivation of the catalyst.

3.3. Reaction pathways of phenylchlorogermane formation

Germanium can readily react with copper(I) chloride to form tetrachlorogermane and a copper–germanium alloy above 240 °C (equation (2)) [6]. We have reported that the reaction of metallic germanium and tetrachlorogermane gave dichlorogermylene intermediate, which further reacts with butadiene [7] and chlorobenzene [8] to afford 1,1-dichlorogermacyclopent-3-ene (equation (3)) and phenyltrichlorogermane (equation (4)), respectively. These facts strongly suggest that the reactions shown in equations (2) and (4) proceed in the germanium chlorobenzene reaction using copper(I) chloride. As shown in figure 1, at the beginning of the reaction, the germanium conversion rapidly increased and phenyltrichlorogermane was mainly formed. Additionally, the X-ray diffraction (XRD) pattern of the mixture of metallic germanium and copper(I) chloride after the 4 h reaction showed the formation of Cu_3Ge alloy phase, as shown in figure 5(a).



$Ge + GeCl_4 \rightarrow GeCl_2$ (3)

$C_6H_5GeCl_3$ (4)

These indicate that the reactions in equations (2) and (4) mainly occurred to form phenyltrichlorogermane and stopped at 4 h. Tetrachlorogermane was not detected probably because it has been quickly converted to the dichlorogermylene intermediate. After 4 h, the conversion slowly increased, and diphenyldichlorogermane was formed as well as phenyltrichlorogermane; *i.e.*, 34 and 23% of the germanium charged were converted to diphenyldichlorogermane and phenyltrichlorogermane, respectively. It is very plausible that the direct reaction of germanium with chlorobenzene almost exclusively proceeds after 4 h. Thus, in the direct synthesis of phenylchlorogermanes, diphenyldichlorogermane is the main product. This is consistent with the fact that diorganodichlorogermane is the main product in the direct synthesis of methylchlorogermanes [1–4]. The consumption rate of germanium is lower than that by the reaction of germanium and copper(I) chloride.

With the use of 20 wt% of copper(II) chloride, at the beginning of the reaction, the sole product was phenyltrichlorogermane, strongly suggesting that only the reaction shown in equation (4) occurred; *i.e.*, the direct synthesis did not proceed. After 4 h, chlorobenzene starts to directly react with germanium since both phenyltrichlorogermane and diphenyldichlorogermane were formed. As shown in figure 5(b), the XRD experiment of the reacted mixture of germanium and copper(II) chloride revealed the formation of the alloy phase. This also indicates the direct formation of phenylchlorogermanes from metallic germanium after 4 h reaction.

The actual active phase of phenylchlorogermane formation is not clear. If we take the phase to be Cu_3Ge as an example, the copper–germanium bond energy, E(Cu–Ge), is estimated using equation (5) as follows [9]. Using the germanium–germanium bond energy, E(Ge–Ge), and the copper–copper bond energy, E(Cu–Cu), of 45.0 and 17.1 $\mathrm{kcal\,mol^{-1}}$, respectively [10], and the enthalpy of formation (ΔH_f) for Cu_3Ge of $-2.00\ \mathrm{kcal\,mol^{-1}}$ [11], E(Cu–Ge) was calculated to be 29.0 $\mathrm{kcal\,mol^{-1}}$. This indicates that the alloy formation leads to weakening the bond energy, which is one of the reasons for the superiority of copper for phenylchlorogermane formation:

$$\Delta H_f = E(\text{Cu–Ge}) - 1/2(E(\text{Ge–Ge}) + E(\text{Cu–Cu})). \quad (5)$$

Figure 5(c) shows an XRD pattern of the reaction mixture after 15 h reaction. Only peaks assigned to germanium metal were observed. No peaks of silver(I) chloride strongly suggests conversion of all silver(I) chloride to a silver–germanium alloy. When silver(I) chloride was used, a long induction period was observed, indicating that the rate of the reaction between germanium and silver(I) chloride is lower than those between germanium and the copper chlorides. Once a silver–germanium alloy was formed, silver played the role of a very active catalyst; however, the deactivation occurred quickly and caused the reaction to stop below 50% germanium conversion.

The reaction pathways using metal chloride catalysts are shown in the equation

$$\mathrm{Ge} + \mathrm{MCl}_n \rightarrow \begin{cases} \mathrm{GeCl_4} \xrightarrow{\mathrm{Ge}} \mathrm{GeCl_2} \xrightarrow{\mathrm{C_6H_5Cl}} \mathrm{C_6H_5GeCl_3} \\ \qquad \text{at the beginning of the reaction} \\ + \\ \text{M–Ge alloy} \xrightarrow{\mathrm{C_6H_5Cl}} (\mathrm{C_6H_5})_2\mathrm{GeCl_2} \\ \qquad \text{the direct synthesis} \\ \qquad + \mathrm{C_6H_5GeCl_3} \end{cases} \tag{6}$$

$$\mathrm{M} = \mathrm{Cu}^{+}, \mathrm{Cu}^{2+}, \mathrm{Ag}^{+}.$$

4. Conclusions

Copper(I) chloride was the most active catalyst for the direct synthesis of phenylchlorogermanes. At the beginning of the reaction, the reaction of metallic germanium and metal chloride resulted in the formation of dichlorogermylene *via* tetrachlorogermane. Chlorobenzene reacted with the germylene to form phenyltrichlorogermane. Subsequently, germanium and the metal reduced during the germanium–metal chloride reaction formed a metal–germanium alloy, which formed an active area for the formation of phenyltrichlorogermane and diphenyldichlorogermane.

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