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Catalytic conversion of silicon tetrachloride to trichlorosilane for a poly-Si process

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ABSTRACT

Hydrogenation of silicon tetrachloride ($SiCl_4$) to trichlorosilane ($SiHCl_3$) using carbon-based catalysts is studied. The results show that surface functional groups that result from the defect sites of the carbon catalysts play an important role in producing $SiHCl_3$. Because the metal–carbon composites obtained by treating sucrose and transition metals at high temperature in the N_2 flow have more defect sites, they display an increased $SiHCl_3$ yield. Elemental analysis of the catalyst and reaction results demonstrate that there is a very good correlation between the $SiHCl_3$ yield and the amount of deposited silicon during the induction time, and the $SiHCl_3$ yield and the accumulated amount of deposited Si species rapidly change initially and then reach a stable value. Hydrogenation of $SiCl_4$ to $SiHCl_3$ in metal-grade silicon (mg–Si) powder is known to give a higher equilibrium conversion of $SiCl_4$. In a similar way, by introducing Si powder into the catalyst bed, a higher $SiHCl_3$ yield can be obtained. It is important to retard the reverse reaction rate of HCl and $SiHCl_3$ to increase the $SiHCl_3$ yield; therefore, the HCl concentration in the product stream should be reduced as soon as it is formed on the catalyst surface during the hydrogenation of $SiCl_4$. Consequently, the Si-doped metal–carbon composite catalyst shows a higher $SiHCl_3$ yield than that of the physically-mixed catalyst and mg–Si powder. These results offer a quite promising potential for developing a stable and effective $SiCl_4$ hydrogenation catalyst and can promote a deeper understanding of this important poly-Si industry reaction.

1. Introduction

$SiCl_4$ is a major byproduct of polycrystalline silicon (poly-Si) production through the chemical vapor deposition (CVD) process of $SiHCl_3$ (Eq. (1)) [1]. Because a drastic increase in the production capacity of poly-Si in the solar cell industry is expected in the near future, finding an efficient process of converting $SiCl_4$ to $SiHCl_3$ is becoming more important economically, and the reaction of $SiCl_4$ to $SiHCl_3$ has become a focus of recent basic scientific and technological research. At present, there are two conversion processes, the hydrogenation of $SiCl_4$ in the presence of mg–Si (Eq. 2) and in the absence of mg–Si (Eq. (3)) [2]:

$$2SiHCl_3 \rightarrow \text{poly-Si} + SiCl_4 + 2HCl, \quad (1)$$

$$3SiCl_4 + 2H_2 + \text{mg-Si} \rightarrow 4SiHCl_3, \quad (2)$$

$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl. \quad (3)$$

The former hydrogenation process (Eq. (2)) involves the use of mg–Si, $SiCl_4$, and H_2 at reaction temperatures ranging from 600 to 700 °C and highly elevated pressures. This process has the drawback of purifying $SiHCl_3$ through a process that involves contamination due to the transition metal impurities of mg–Si. The latter hydrogenation process (Eq. (3)) involves a thermal reaction of $SiCl_4$ and H_2 at temperatures exceeding 1000 °C, and the main disadvantages of this process are the high energy consumption and undesirable chlorosilane products that result from the high reaction temperature [2]. Therefore, it is necessary to develop suitable catalysts that enable a reduction of the reaction temperature and do not bring impurities to the process. Some efficient catalysts have been reported.

Transition metal silicides, formed by the reaction of the metal with $SiCl_4$–H_2 mixtures under hydrogenating reaction conditions, are known to allow a substantial lowering of the reaction temperature of the hydrogenation of $SiCl_4$ as compared with the uncatalyzed reaction [3–6]. Ingle and Peffley reported copper

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hydride as an active catalyst, which reacted with $SiCl_4$ to form copper chloride and $SiHCl_3$, and the process parameters affecting $SiHCl_3$ yields [7]. Meanwhile, Gusev et al. offered a plasma process as well as a catalytic hydrogenation process, and they concluded that the pressure in the reaction zone played a key role in determining the $SiHCl_3$ yield of $SiCl_4$ plasma hydrogenation [8,9].

When dealing with transition metals in a catalytic reaction containing chlorine, it is important to note whether the metals are removed from the solid phase in the form of volatile metal chlorides or the silicide catalysts are stable under the reaction conditions. Therefore, Acker and Bohmhammel reported the thermodynamics results of transition metal silicides and suggested that these can be formed in situ by reaction of metal with a $SiCl_4/H_2$ atmosphere (Eq. 4) [3]. They also indicated that the reaction conditions have to be chosen in such a way that the silicon is removed only to a small extent from the silicide phases:

$$xSiCl_4 + 2xH_2 + yM \rightarrow M_ySi_x + 4xHCl. \quad (4)$$

As mentioned above, the hydrogenation of $SiCl_4$ in the absence of mg–Si is carried out at high temperatures ($>1000\ ^\circ C$). There have been many trials to develop a novel catalyst to allow the reaction temperature to be decreased without $SiHCl_3$ yield loss, but no notable results have been reported yet. Meanwhile, in the hydrogenation of $SiCl_4$ in the presence of mg–Si, even though it is considered that mg–Si reacts with HCl to give additional $SiHCl_3$, a higher $SiHCl_3$ yield can be obtained by introducing CuCl to the mg–Si or using mg–Si with a certain impurity level of copper or iron [7], because these metals or metal chlorides are known to catalyze the reaction. However, other impurity metals, such as boron, phosphorus, or aluminum, which have low boiling points of their chlorides, contaminate the pure chlorosilane products, even though the reaction is carried out under high pressure (>20 atm).

Much attention has been focused on the synthesis of structured carbons using template synthesis techniques [10], and they have been studied for some applications as catalyst supports [11–13]. However, in spite of many efforts, these carbons have not been reported to be used industrially as a catalyst material. Choi and Woo initiated a study to synthesize a metal–carbon composite by pyrolysis of metal and carbon precursors in a removable silica template [14]. They reported that aggregation and movement of metal precursors are hindered by the polymerization of carbon precursors, and the composite can be successfully used as a catalyst.

Our approach in this work is split into two major sections. In the first section, the metal–carbon composites as a $SiCl_4$ hydrogenation catalyst are synthesized and characterized in order to investigate the main factors affecting $SiHCl_3$ yield. In the other section, Si-doped metal–carbon composites obtained by decomposing SiH_2Cl_2, which are byproducts of the $SiHCl_3$ CVD reaction, are presented and a plausible explanation is given for the higher $SiHCl_3$ yield.

2. Experimental

2.1. Apparatus

The apparatus used in the reaction experiment is shown schematically in Fig. 1. The catalyst was placed on a fritz plate positioned inside a vertical quartz tube (inner diameter 8.7 mm). $SiCl_4$ was introduced into the reactor tube from a $SiCl_4$ bubbler by bubbling purified H_2 through the $SiCl_4$ solution. The molar ratio of the $H_2/SiCl_4$ feed stream could be conveniently selected by adjusting the $SiCl_4$ temperature. Since the vapor pressure of the $SiCl_4$ liquid is constant at a given temperature, the $H_2/SiCl_4$ feed ratio remains constant even though the H_2 flow rate varies. An in-line gas chromatograph (HP 6890) was connected to the outlet of the hydrogenation reactor. The analytical column was 1/8 in. O.D. × 12 ft. packed with a 5% SE-30 silicon gum stationary phase on 150 mesh Chromosorb W. The $SiHCl_3$ yield of the prepared catalysts was initially increased and reached a stable value.

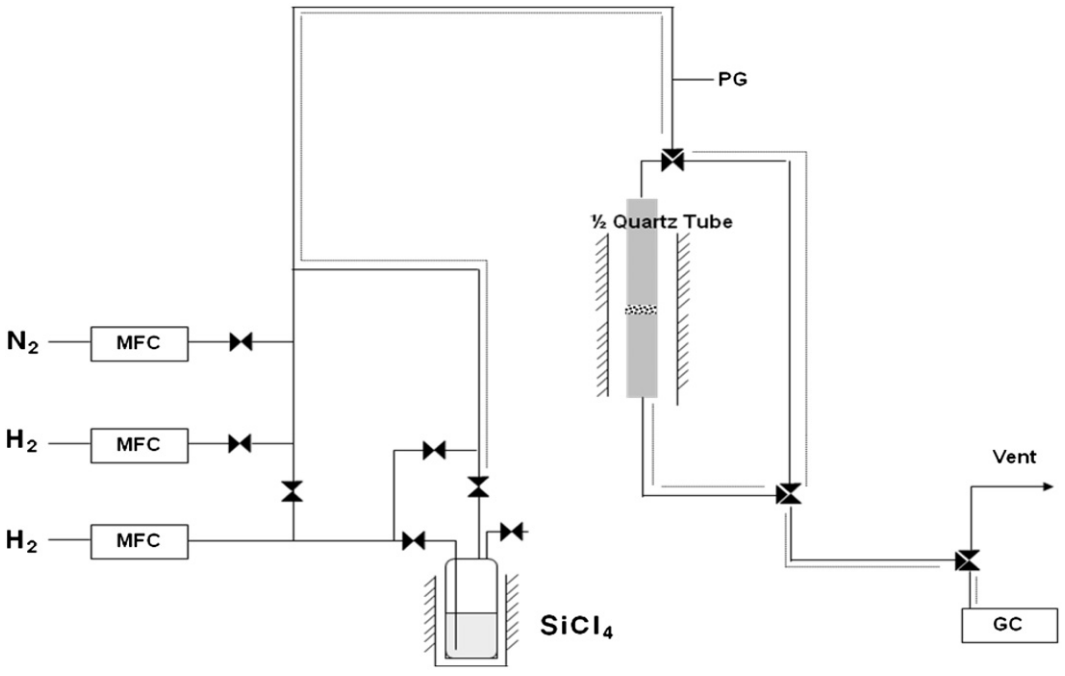

Fig. 1. Schematic drawing to illustrate the catalytic hydrogenation of $SiCl_4$.