



# Catalytic chlorination of methylphenyldichlorosilane with gaseous chlorine to chlorinated methylphenyldichlorosilanes over Lewis acids



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## ABSTRACT

Methylchlorophenyldichlorosilane (MeClPhSiCl<sub>2</sub>) and methyldichlorophenyldichlorosilane (MeCl<sub>2</sub>PhSiCl<sub>2</sub>) were synthesized by the catalytic chlorination of methylphenyldichlorosilane (MePhSiCl<sub>2</sub>) with Cl<sub>2</sub> over Lewis acid catalysts. The catalytic activities of Lewis acid catalysts were in an order of FeCl<sub>3</sub> > SbCl<sub>5</sub> > AlCl<sub>3</sub> > SnCl<sub>4</sub>. However, FeCl<sub>3</sub> also highly catalyzed the cleavage of chlorophenyl–silicon bond to form chlorobenzene. At a low mole ratio of SbCl<sub>5</sub> to MePhSiCl<sub>2</sub> of 1.4 × 10<sup>-5</sup>:0.45, the yield of MeClPhSiCl<sub>2</sub> was around 60% after reacting at 25–100 °C for 15–20 h. At a high mole ratio of 1.4 × 10<sup>-4</sup>:0.45, the yield of MeCl<sub>2</sub>PhSiCl<sub>2</sub> reached 44% after reacting at 80–100 °C for 20 h.

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## 1. Introduction

Organopolysiloxane oils have been widely used in lubricant, coating, pharmaceutical, cosmetic, and food industries because of their unique properties, such as low surface tension, good lubricity, high chemical and thermal stability, excellent weather resistance, fine electrical insulation, and non-toxicity [1–5]. Chlorinated organopolysiloxane oils have good lubricating and flameproof characteristics. Particularly, chlorinated phenyl or chlorinated alkyl radical-containing organopolysiloxanes have good lubricity under high pressure at both extremely high and low temperatures, as compared to conventional organopolysiloxanes, in which alkyl and phenyl radicals are free of any nuclear bonded chlorine atom [6–9]. Chlorinated phenyl-containing organopolysiloxanes can protect steel and brass from wearing and eroding under load at temperatures ranging from below –70 °C and above 260 °C, leading to their wide use in electronics and aerospace engineering [10].

Several groups have studied the chlorination reactions of organochlorosilane monomers [9–15]. It is well known that chlorinated alkyl-containing organochlorosilanes are usually synthesized by the photochemical chlorination of alkylchlorosilanes with commercial chlorine [11,12]. For the synthesis of chlorinated phenyl-containing organochlorosilanes, Burkhard [9]

reported the synthesis of methylchlorophenyldichlorosilane by the Grignard reaction between chlorophenylmagnesium bromide and methyltrichlorosilane. However, Grignard reagents are usually synthesized in environmentally harmful solvents, such as diethyl ether and tetrahydrofuran. In the viewpoint of environment and cost, an optional method for the synthesis of chlorinated phenyl-containing organochlorosilanes is the direct chlorination of phenyl-containing organochlorosilanes with gaseous chlorine catalyzed by Lewis acid catalysts [10,13–15]. Rochow [13] first reported the synthesis of chlorinated diphenyl-containing organodichlorosilanes by the chlorination of diphenyldichlorosilane with gaseous chlorine using SbCl<sub>5</sub> or iron powder as catalysts. Holdstock [14,15] investigated the chlorination of phenyltrichlorosilane with gaseous chlorine to chlorinated phenyl-containing organotrichlorosilanes catalyzed by AlCl<sub>3</sub>, FeCl<sub>3</sub>, SbCl<sub>5</sub>, and iron powder with or without carbon tetrachloride as a solvent. By comparing the results, it is found that the use of solvent in the chlorination reaction is not necessary [14,15]. On the other hand, the chlorination reaction of phenyl-containing organochlorosilanes with gaseous chlorine catalyzed by Lewis acid catalysts is accompanied with the cleavage of chlorophenyl–silicon bonds, causing the formation of chlorinated benzenes as by-products and subsequently lowering the yield of chlorinated phenyl-containing organochlorosilanes [14]. To the best of our knowledge, the effect of the type of Lewis acid catalysts and experimental conditions on the yields of chlorinated organochlorosilanes and the cleavage extent of phenyl–silicon bonds was not investigated in detail until now. Therefore, it is worthy of further investigation to discover

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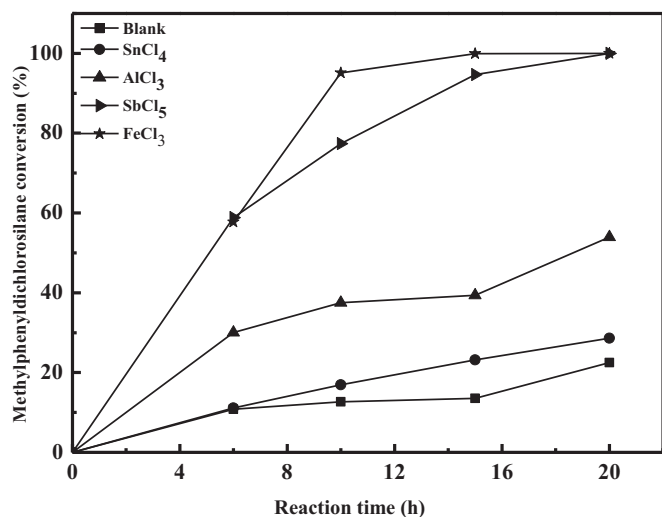


Fig. 1. Conversion of methylphenyldichlorosilane catalyzed by Lewis acid catalysts with the catalyst loading of  $1.4 \times 10^{-4}$  mol at the reaction temperature of 50 °C.

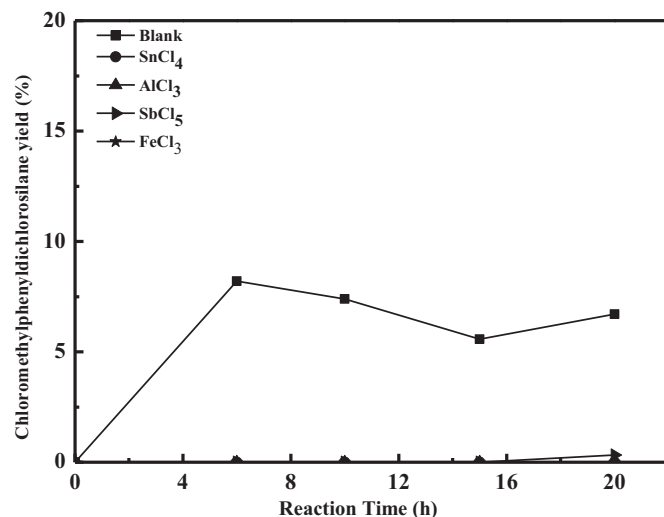


Fig. 3. Yield of chloromethylphenyldichlorosilane in the chlorination reaction of methylphenyldichlorosilane catalyzed by Lewis acid catalysts with the catalyst loading of  $1.4 \times 10^{-4}$  mol at the reaction temperature of 50 °C.

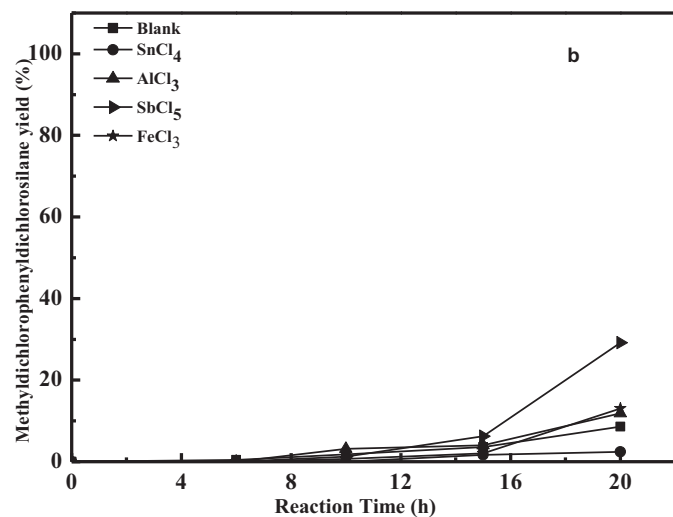
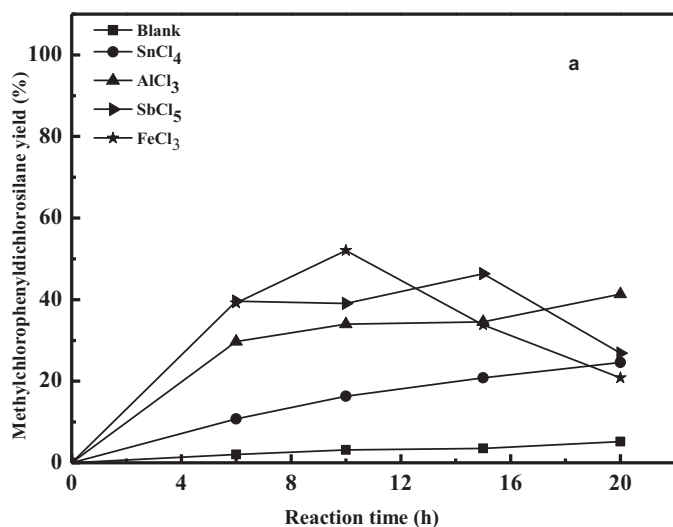


Fig. 2. Yields of (a) methylchlorophenyldichlorosilane and (b) methyldichlorophenyldichlorosilane in the chlorination reaction of methylphenyldichlorosilane catalyzed by Lewis acid catalysts with the catalyst loading of  $1.4 \times 10^{-4}$  mol at the reaction temperature of 50 °C.

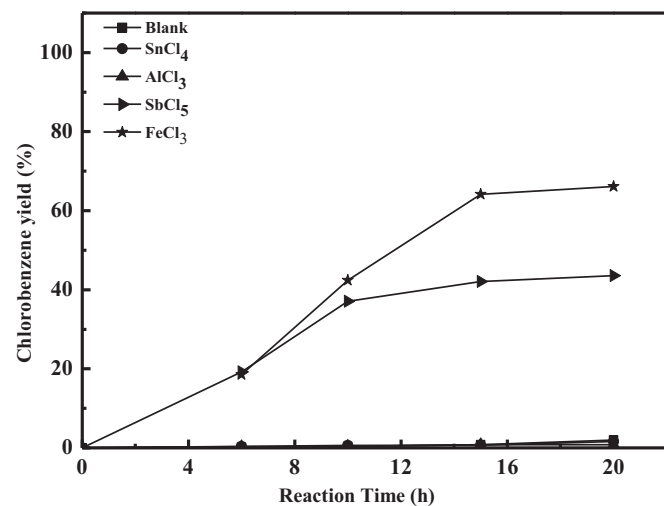


Fig. 4. Yield of chlorobenzene in the chlorination reaction of methylphenyldichlorosilane catalyzed by Lewis acid catalysts with the catalyst loading of  $1.4 \times 10^{-4}$  mol at the reaction temperature of 50 °C.

how to improve the chlorination reaction between phenyl-containing organochlorosilanes and gaseous chlorine over Lewis acid catalysts.

In our present work, we report the synthesis of methylchlorophenyldichlorosilane (MeClPhSiCl<sub>2</sub>) and methyldichlorophenyldichlorosilane (MeCl<sub>2</sub>PhSiCl<sub>2</sub>) by the chlorination of methylphenyldichlorosilane (MePhSiCl<sub>2</sub>) with gaseous chlorine catalyzed by Lewis acid catalysts, such as SbCl<sub>5</sub>, SnCl<sub>4</sub>, FeCl<sub>3</sub>, and AlCl<sub>3</sub>. The effect of reaction parameters, such as reaction temperature, reaction time, and catalyst loading, on the chlorination reaction was investigated in detail. MeClPhSiCl<sub>2</sub> and MeCl<sub>2</sub>PhSiCl<sub>2</sub> were produced as the main products over the Lewis acid catalysts. At a low catalyst loading level, SbCl<sub>5</sub> showed high catalytic activity toward the formation of MeClPhSiCl<sub>2</sub> and MeCl<sub>2</sub>PhSiCl<sub>2</sub>. The reaction routes were also briefly discussed.

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