

Methylation of methyltrichlorosilane with methyl chloride over active metals and activated carbon

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Abstract—Gas phase methylation of methyltrichlorosilane with methyl chloride to high-valued dimethyldichlorosilane was carried out by using metallic aluminum as a chlorine acceptor in the co-presence of activated carbon, tin, and zinc. The addition of activated carbon in metallic aluminum significantly enhanced the methylation of methyltrichlorosilane, and dimethyldichlorosilane was dominantly produced. Activated carbon played a catalyst role in the methylation reaction. When active metals, such as tin and zinc, were added in the mixture of aluminum and activated carbon, the active metals and activated carbon synergistically catalyzed the methylation of methyltrichlorosilane with methyl chloride toward the formation of dimethyldichlorosilane.

Key words: Alkylation, Chlorinated Hydrocarbon, Aluminum, Activated Carbon

INTRODUCTION

Methylchlorosilanes are produced in fluidized bed reactor by the Rochow direct synthesis reaction of solid silicon with gaseous methyl chloride. In addition to the formation of the desirable dimethyldichlorosilane and trimethylchlorosilane, methyltrichlorosilane, dimethylhydrochlorosilane, methylhydrodichlorosilane, and methylchlorodisilanes are also produced as by-products [1-4]. The weight percentage of by-products was *ca.* 15-20% of crude products. Among the by-products, methyltrichlorosilane is *ca.* 10 wt% of crude products, which is rarely used in organosilicon industry. Methyltrichlorosilane is mainly used to prepare pyrogenic silica. This process is an unsatisfactory solution because valuable methyl groups are turned to CO₂ and water.

It has been reported that methyltrichlorosilane can be converted to high-valued dimethyldichlorosilane *via* the redistribution reaction with methyl-enriched silanes, such as tetramethylsilane and trimethylchlorosilane. But the weight percentages of tetramethylsilane and trimethylchlorosilane were *ca.* 3% and 1% of crude products, respectively. The amount of methyl-enriched silanes present in by-products cannot balance that required in the redistribution reaction in industrial practice.

It was disclosed that chlorine-enriched methylchlorosilanes were alkylated by passing the methylchlorosilanes and alkyl halide over aluminum, zinc or other active metals at temperatures of 300-500 °C [5,6]. In the reaction, chlorine groups on the methylchlorosilanes were replaced by alkyl groups from alkyl halide, and the active metals served as chlorine acceptors to form metal halides. For example, when pure methyltrichlorosilane and methyl chloride with a mole ratio of 1 : 1 were passed over aluminum, in the resultant mixture the compositions of trimethylchlorosilane and dimethyldichlorosilane were increased from 6.3% to 21% and from 4.5% to 11%, re-

spectively, with increasing the reaction temperatures from 350 to 450 °C [6]. To obtain high conversion of methyltrichlorosilane in the methylation reaction, metallic tin, alumina, silica, and activated carbon were used as additives in an aluminum bed [7]. It was found that when the methylation between methyltrichlorosilane and methyl chloride (mole ratio of 1 : 3) over tin-catalyzed aluminum fixed bed was carried out at 300 °C with a residence time of 5 seconds, the conversion of methyltrichlorosilane was *ca.* 5% with a tetramethylsilane selectivity of more than 93%. When alumina, silica, and carbon were added in the fixed bed, the conversions of methyltrichlorosilane were increased to 9.5%, 22.1%, and 48.6%, respectively, but the product selectivity was also significantly changed [7].

To convert methyltrichlorosilane to high-valued dimethyldichlorosilane and trimethylchlorosilane, methylation of methyltrichlorosilane by reacting with methyl chloride and using aluminum as a chlorine acceptor is an alternative to the redistribution process. However, the methylation reaction is seldom reported and the reaction mechanism has not been well established until now. The methylation of methyltrichlorosilane with methyl chloride over aluminum-based chlorine acceptor is worthy of further investigation.

In the present work, we report the methylation of methyltrichlorosilane with methyl chloride over aluminum-based chlorine acceptor. The effect of experimental parameters, such as reaction temperature, amount of activated carbon, and active metal catalysts was investigated in detail. The presence of activated carbon significantly enhanced the methylation of methyltrichlorosilane to dimethyldichlorosilane at a lower reaction temperature. The methylation mechanism was also discussed briefly.

EXPERIMENTAL

1. Chemicals

Methyltrichlorosilane (99%) and methyl chloride (99.9 %) were kindly provided by Jiangsu Hongda New Materials Co., Ltd. Needle-like aluminum powders (0.38-0.83 mm × 0.7-1.5 mm, 99.5%) were

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purchased from Henan Yanshi Jinhua Metallurgy Materials Plant. Zinc (1-13.5 μm , 99%), tin (3.5-50 μm , 99%), and activated carbon powders (0.5-1.2 mm) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nitrogen (99.999 %) was purchased from Suzhou Jinhong Gas Co., Ltd. All the chemicals were used as received without further purification.

2. Methylation of Methyltrichlorosilane

A stainless steel fixed bed reactor with a diameter of 16 mm and a length of 450 mm was charged with 90 mL of aluminum powders and other additives, such as activated carbon, zinc, and tin powders. The weight ratios of activated carbon to aluminum powders were 5% and 20%, respectively. The weight ratios of zinc and tin to aluminum were 3% and 0.2%, respectively. The flow rates of methyl chloride and N_2 were 16 mL/min and 20 mL/min, respectively. The flow rate of liquid methyltrichlorosilane was 0.1 mL/min. The mole ratio of methyltrichlorosilane to methyl chloride was 1 : 1.1. The reaction mixtures were passed through a stainless steel evaporator at 220 °C and the liquid methyltrichlorosilane was evaporated. The heated gas was introduced into the fixed bed reactor and reacted at different temperatures. The vapor exiting the reactor was passed through a heated trap at *ca.* 100 °C, to remove AlCl_3 from the vapor stream as a solid. The products were cooled and collected in an ice bath for analysis.

All the collected reaction products were analyzed on a gas chromatograph equipped with flame ionization detector (FID) and an OV1701 capillary column (0.25 mm \times 30 m). The compositions of the reaction products were analyzed by internal standard method. The conversion of methyltrichlorosilane and the yields of dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane were calculated according to the following equations:

$$X_M = [M]_{in} - [M]_{out} / [M]_{in}$$

$$Y_M = [M]_{out} / [M]_{in}$$

where, M1 referred to methyltrichlorosilane; Mi referred to dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane present in products.

RESULTS AND DISCUSSION

1. Effect of Active Metals on Methylation of Methyltrichlorosilane

Fig. 1 shows the conversion of methyltrichlorosilane and the yields of dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane in the methylation of methyltrichlorosilane using pure aluminum, aluminum and tin, and aluminum and zinc as chlorine acceptors, respectively, at different reaction temperatures. When pure aluminum was used as the chlorine acceptor, the conversion of methyltrichlorosilane was around 1.5% at reaction temperatures ranging from 230 to 320 °C. Dimethyldichlorosilane was formed as a main product with a yield *ca.* 1.4%. Trimethylchlorosilane and tetramethylsilane were also detected with the yields of less than 0.2%. When tin powder was used as an additive in aluminum chlorine acceptor, the conversion of methyltrichlorosilane and the yield of dimethyldichlorosilane were slightly increased to 1.9% and 1.8%, respectively. Trace amount of trimethylchlorosilane and tetramethylsilane was also detected. When zinc powder was added as an additive in aluminum chlorine acceptor, the conversion of methyltrichlorosi-

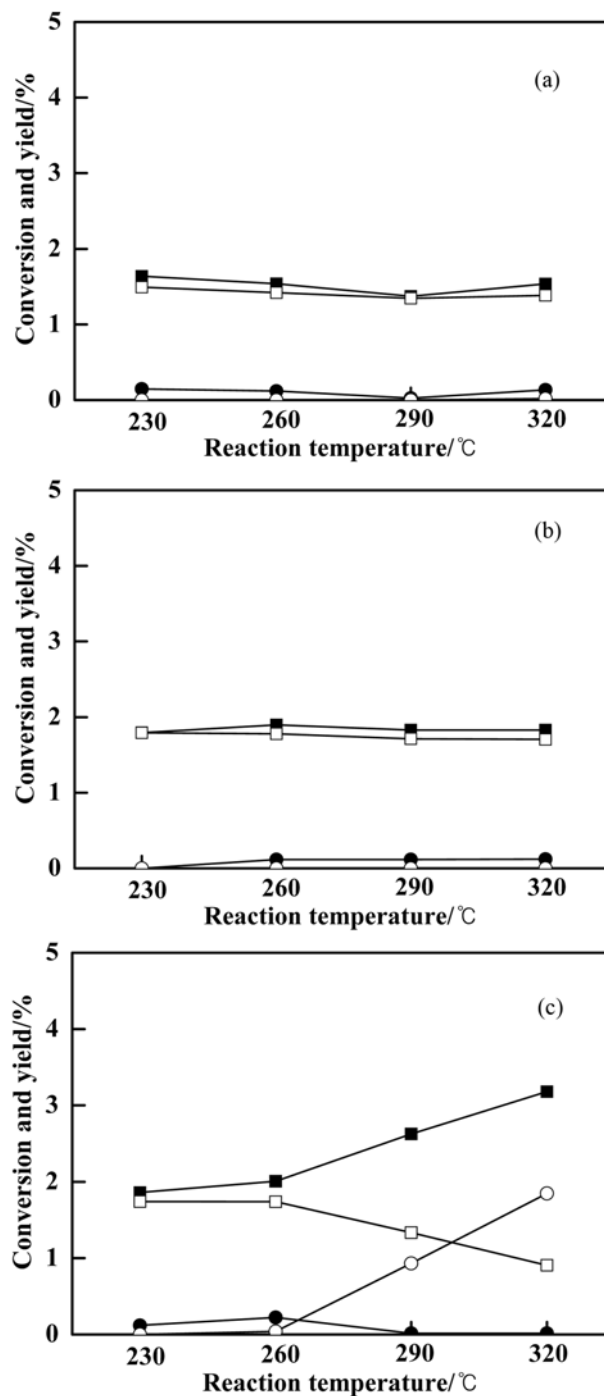
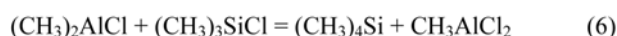
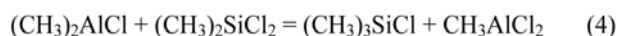
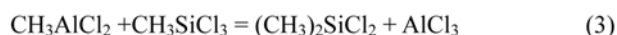
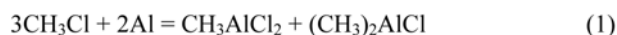


Fig. 1. The conversion of methyltrichlorosilane and the yields of dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane at different reaction temperatures using (a) pure aluminum, (b) aluminum and tin with a weight ratio of tin to aluminum of 0.2%, and (c) aluminum and zinc with a weight ratio of zinc to aluminum of 3% as chlorine acceptors, respectively. ■, the conversion of methyltrichlorosilane; □, the yield of dimethyldichlorosilane; ●, the yield of trimethylchlorosilane; ○, the yield of tetramethylsilane.

lane was increased from 1.9% to 3.2% with increasing the reaction temperatures from 230 to 320 °C. The yield of dimethyldichlorosilane was decreased from 1.7% to 0.9%. The yield of tetramethylsi-

lane reached 1.9% when the reaction temperature was 320 °C. The presence of tin promoted the methylation of methyltrichlorosilane [7]. The addition of zinc not only promoted the methylation of methyltrichlorosilane but also changed the selectivity of the resultant methyl-enriched methylchlorosilanes. Although it was suggested that tin and zinc catalyzed the methylation of methyltrichlorosilane with



Scheme 1. Methylation of methyltrichlorosilane with methyl chloride by using metallic aluminum as a chlorine acceptor.

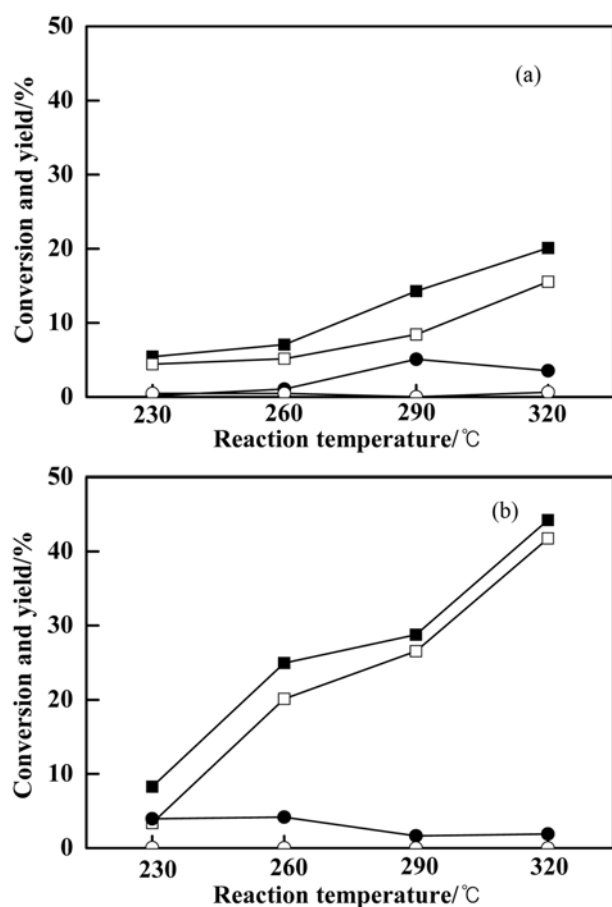
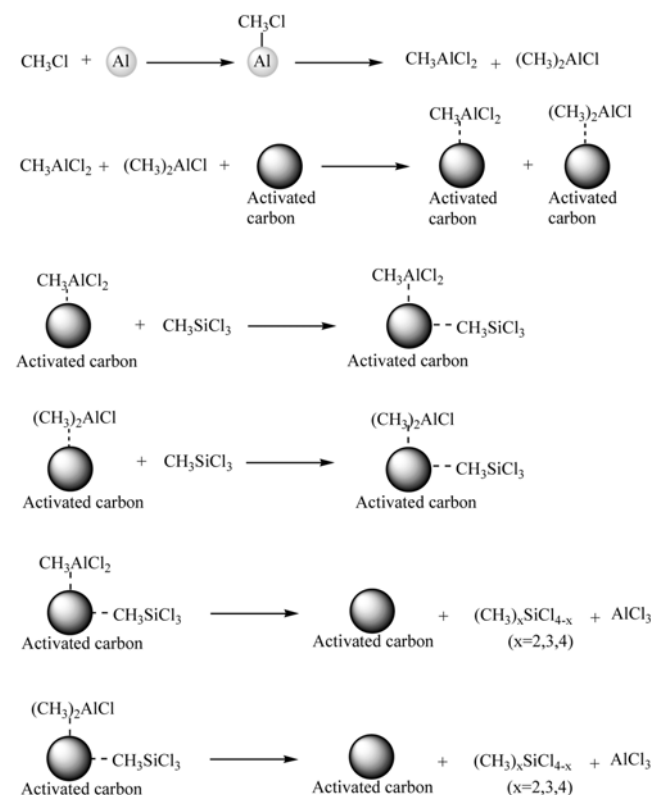


Fig. 2. The conversion of methyltrichlorosilane and the yields of dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane using aluminum powders as chlorine acceptors in the presence of (a) 5% and (b) 20% activated carbon. ■, the conversion of methyltrichlorosilane; □, the yield of dimethyldichlorosilane; ●, the yield of trimethylchlorosilane; ○, the yield of tetramethylsilane.

methyl chloride when aluminum powders were used as chlorine acceptors, the catalytic activity of the active metals was not significant under our present experimental conditions. Interestingly, instead of the methylation of methyltrichlorosilane, large amount of methyl aluminum sesquichloride was dominantly formed. For example, when pure aluminum was used as the chlorine acceptor at a reaction temperature of 320 °C, the content of the resultant methyl aluminum sesquichloride was *ca.* 88% of the products, which was calculated according to the GC peak areas. It was suggested that aluminum powders firstly reacted with methyl chloride to form methyl aluminum sesquichloride. Then the resultant methyl aluminum sesquichloride reacted with methyltrichlorosilane to form dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane, subsequently. Methyl aluminum sesquichloride was finally converted to aluminum chloride. The reaction routes are illustrated in Scheme 1.

2. Effect of Activated Carbon on Methylation of Methyltrichlorosilane

Fig. 2 shows the effect of activated carbon on the methylation of methyltrichlorosilane with methyl chloride using metal aluminum as a chlorine acceptor. When activated carbon was added in aluminum powders with a weight ratio of activated carbon to aluminum of 5%, the conversion of methyltrichlorosilane was increased from 5.4% to 20.1% with increasing the reaction temperatures from 230 to 320 °C. The yields of dimethyldichlorosilane and trimethylchlorosilane were increased from 4.4% to 15.5% and from 0.2% to 3.5%, respectively. Trace amount of tetramethylsilane was formed. When



Scheme 2. The possible reaction mechanism of methylation of methyltrichlorosilane with methyl chloride using metallic aluminum as a chlorine acceptor in the presence of activated carbon.

the weight ratio of activated carbon was increased to 20%, the conversion of methyltrichlorosilane was increased from 8.3% to 44.2% with increasing the reaction temperatures from 230 to 320 °C. The yield of dimethyldichlorosilane was increased from 3.3% to 41.7% and the yield of trimethylchlorosilane was decreased from 3.9% to 1.9%. Trace amount of tetramethylsilane was also formed. Aluminum chloride was formed at the same time. The presence of activated carbon enhanced the methylation of methyltrichlorosilane with methyl chloride to form dimethyldichlorosilane. The possible reaction mechanism was suggested as follows. First, methyl chloride reacted with metallic aluminum to form methyl aluminum sesquichloride. The resultant methyl aluminum sesquichloride and methyltrichlorosilane were adsorbed on the surfaces of activated carbon and activated by activated carbon. The activated species reacted to form methyl-enriched methylchlorosilanes and aluminum chloride. The activated carbon played a catalyst role in the methylation reaction. The possible reaction routes are illustrated as Scheme 2.

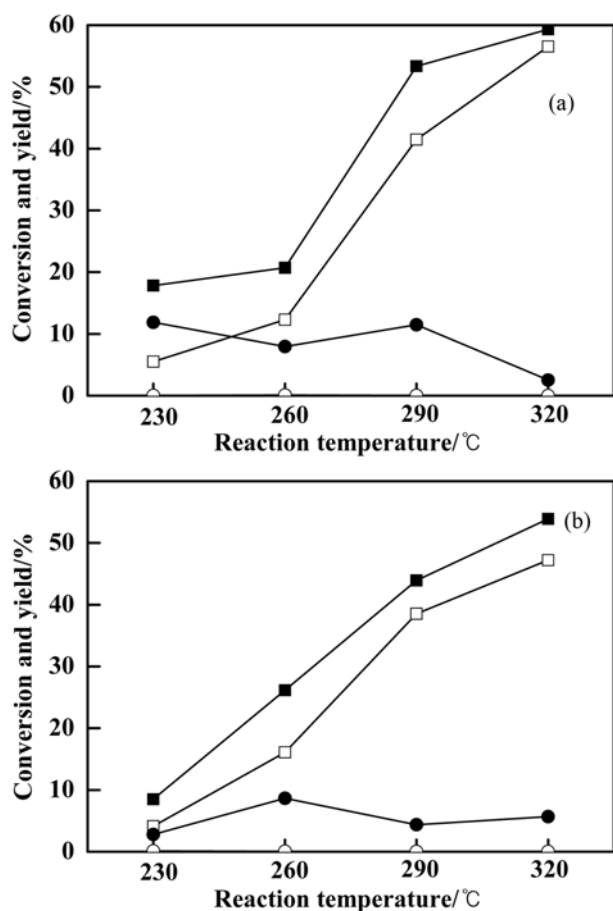


Fig. 3. The conversion of methyltrichlorosilane and the yields of dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane using aluminum powders as chlorine acceptors and (a) tin or (b) zinc as a catalyst in the presence of activated carbon with a weight ratio of activated carbon to aluminum of 20%. The weight ratios of tin and zinc to aluminum were 0.2% and 3%, respectively. ■, the conversion of methyltrichlorosilane; □, the yield of dimethyldichlorosilane; ●, the yield of trimethylchlorosilane; ○, the yield of tetramethylsilane.

3. Synergetic Effect of Active Metal and Activated Carbon on Methylation of Methyltrichlorosilane

We also investigated the effect of active metals, such as tin and zinc, on the methylation of methyltrichlorosilane with methyl chloride by using metallic aluminum as a chlorine acceptor in the presence of activated carbon.

When aluminum, tin, and activated carbon were co-present in the methylation of methyltrichlorosilane with methyl chloride, the conversion of methyltrichlorosilane was increased from 17.8% to 59.3% with increasing the reaction temperatures from 230 to 320 °C (Fig. 3). The yield of dimethyldichlorosilane was increased from 5.5% to 56.5%, and the yield of trimethylchlorosilane was decreased from 11.8% to 2.5% with increasing the reaction temperatures. Trace amount of tetramethylsilane was formed. When aluminum, zinc, and activated carbon were co-present in the methylation of methyltrichlorosilane with methyl chloride, the conversion of methyltrichlorosilane was increased from 8.5% to 53.9% with increasing the reaction temperatures from 230 to 320 °C. The yield of dimethyldichlorosilane was increased from 4.1% to 47.2%, while the yield of tri-

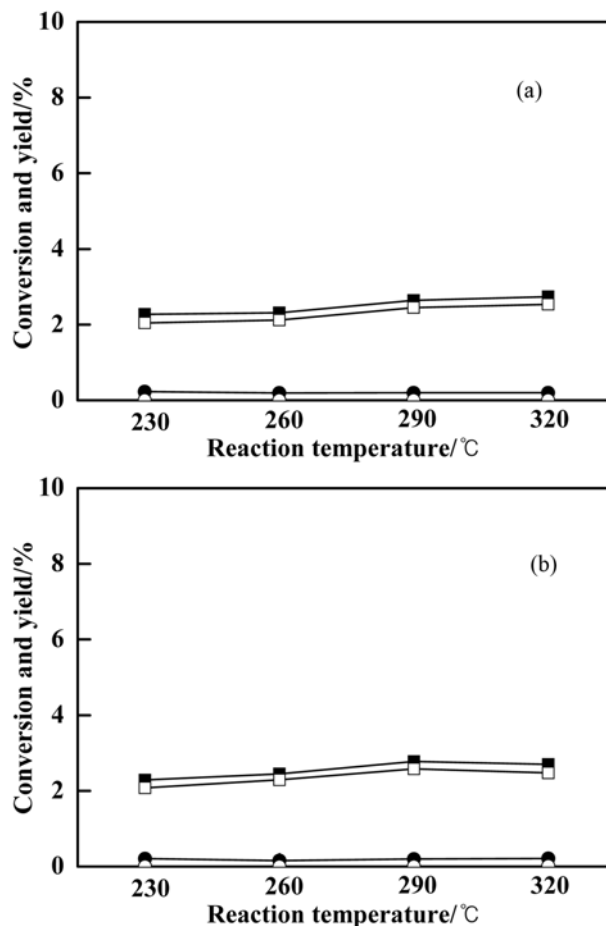


Fig. 4. The conversion of methyltrichlorosilane and the yields of dimethyldichlorosilane, trimethylchlorosilane and tetramethylsilane at different reaction temperatures in an activated carbon bed with (a) tin (0.11 g) and (b) zinc (1.64 g), respectively. ■, the conversion of methyltrichlorosilane; □, the yield of dimethyldichlorosilane; ●, the yield of trimethylchlorosilane; ○, the yield of tetramethylsilane.

methylchlorosilane was around 5% at the reaction temperatures ranging from 230 to 320 °C. Trace amount of tetramethylsilane was also formed. As compared to that using aluminum as a chlorine acceptor in the presence of 20% activated carbon, the addition of tin and zinc increased the conversion of methyltrichlorosilane by more than 9.7%. From controlled experiments (Fig. 4), it was found that the conversion of methyltrichlorosilane was less than 3% when tin and activated carbon or zinc and activated carbon were used in the methylation of methyltrichlorosilane with methyl chloride in the absence of aluminum powders. It is reasonable to conclude that tin (or zinc) and activated carbon synergistically catalyzed the methylation reaction toward the formation of dimethyldichlorosilane when metallic aluminum was used as a chlorine acceptor. The role of tin and zinc was explained as being that tin and zinc present in aluminum powders promoted the reaction between aluminum powders and methyl chloride to form methyl aluminum sesquichloride, subsequently giving high methylation rate of methyltrichlorosilane [8].

CONCLUSIONS

Gas phase methylation of methyltrichlorosilane with methyl chloride to methyl-enriched methylchlorosilanes, such as dimethyldichlorosilane, trimethylchlorosilane, and tetramethylsilane, using metallic aluminum as a chlorine acceptor in the co-presence of activated carbon and tin or zinc, was investigated. When activated carbon (20%) and metallic aluminum were co-present in the methylation reaction system, the conversion of methyltrichlorosilane reached 44.2% at a reaction temperature of 320 °C, and dimethyldichlorosilane was produced as a main product with a maximum yield of 41.7%.

The activated carbon acted as a catalyst in the methylation reaction. When small amount of tin or zinc was added in the mixture of activated carbon and metallic aluminum powders, the conversion of methyltrichlorosilane was increased by more than 9.7% as compared to that using metallic aluminum as a chlorine acceptor and activated carbon as a catalyst. This method has potential practical application in the methylation of the surplus methyltrichlorosilane with facile methyl chloride to valuable dimethyldichlorosilane.

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