Gas Phase Reaction Kinetics in Boron Fibre Production

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In the production of boron fibres using the chemical vapor deposition (CVD) technique, boron deposition and dichloroborane formation reactions occurs simultaneously. Boron deposition reaction occurs at the surface, whereas the formation of dichloroborane is the result of both gas phase and surface reactions. A continuous stirred tank reactor (CSTR) type of reactor was designed to investigate the reaction kinetics and kinetic parameters in the gas phase reactions of boron trichloride and hydrogen. It was concluded that reaction rate of the product increased with an increase in the inlet concentration of both reactants (BCl_3 and H_2) and with an increase in the reactor temperature. While reaction order with respect to BCl_3 was almost constant at about 0.5 at each temperature, reaction order with respect to hydrogen increased significantly at temperatures lower than 350°C. A general rate expression was derived for $BHCl_2$ formation from BCl_3 and hydrogen. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 1562–1569, 2012
Keywords: kinetics, gas phase reaction, dichloroborane, CVD, boron fibres

Introduction

Advanced composite materials, which are lighter, stronger, and stiffer than any other structural materials, have found applications in various areas.[1] Boron fibres and some other boron compounds, like boron carbide and boron nitride, have been increasingly used in composite materials.

Boron is a hard, light, refractory element, located in group III-A in the periodic table and exhibits semiconducting behavior. It has found significant applications in the production of fibre-reinforced composites, protective and refractory coatings, and electronic components. Boron fibres have an average tensile strength of 3.45×10^9 N/m^2 and an elastic modulus of 4.14×10^{11} N/m^2. The density of boron fibre is 2.6 g/cm^3.[1]

Boron fibre can be produced using the chemical vapor deposition technique, with the reaction of BCl_3 or other boron halides with hydrogen gas on a hot metal substrate.[2–7] In this process, mass transfer, surface reaction, and gas phase reaction kinetics affect the boron deposition rate on the hot substrate.[8–10] Besides boron, the reaction products are hydrochloric acid and dichloroborane ($BHCl_2$). Two independent overall reactions were considered for the formation of boron fibre in such a CVD reactor. In other words, boron and dichloroborane formation reactions take place simultaneously in the reactor.[11,12] While the boron formation reaction takes place on the substrate surface (Rxn 1), the dichloroborane formation reaction (Rxn 2) occurs both on the substrate surface and also in the gas phase.[11] Detailed analysis of the reaction mechanism and the proposed rate expressions for hydrogen reduction of BCl_3 on a hot substrate surface were reported in our earlier publication.[12]

$$2BCl_3(g) + 3H_2(g) \rightarrow 2B(s) + 6HCl(g) \qquad \text{(Rxn 1)}$$

$$BCl_3(g) + H_2(g) \rightarrow BHCl_2(g) + HCl(g) \qquad \text{(Rxn 2)}$$

Information about the gas phase reaction kinetics and mass transfer is also needed for the complete analysis of the CVD reactor, designed for boron fibre production. Gas phase reaction is important to determine boron film growth rate. In

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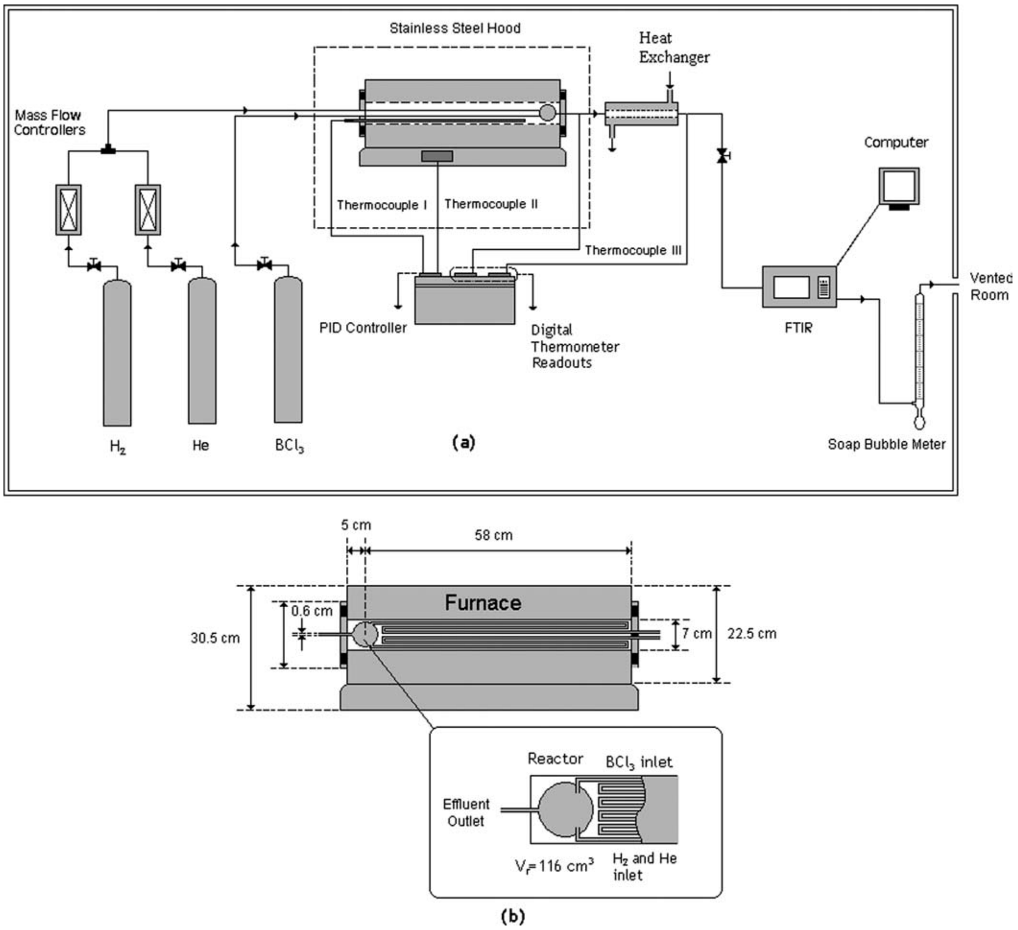

Figure 1. (a) Schematic drawing of the experimental apparatus and (b) Details of continuous stirred tank reactor.

the gas phase reaction, highly reactive intermediate species may form and these intermediates are reported to play important role in the CVD process.[13]

There is no published work related to the gas phase reactions taking place in boron fibre produced by the reaction of hydrogen and boron trichloride. The objective of the present effort is to study the gas phase reactions in the production of boron fibre from boron trichloride and hydrogen gases. For this purpose, a continuous well mixed reactor was designed and used to obtain reliable experimental kinetic data for dichloroborane formation in the gas phase. Such data is essential for the design of a CVD reactor.

Experimental

A continuous stirred reactor was constructed to obtain kinetic data for dichloroborane formation from boron trichloride and hydrogen. Figure 1 shows a sketch of the experimental apparatus. Preheated BCl_3 and H_2 gases entered the spherical reaction chamber of the apparatus as shown in Figure 1b. In addition to boron trichloride and hydrogen, helium gas was used to purge the system before and after each run. Flow rates of hydrogen and diluent helium gases were adjusted using mass flow controllers and the flow rate of boron trichloride gas was adjusted by a needle valve. These gases flowed through $^1/_4$-in stainless steel tubing some part of which was coiled and placed into a furnace so that the gas temperature reached the desired reactor temperature. The reactant gases BCl_3 and H_2 entered the reactor separately in such a way that a well mixing of the reactants is provided (Figure 1b). The spherical reactor, which has a volume of 116 cm^3, was made of stainless steel and placed to the end of the furnace. The reactor temperature was measured with a Type K thermocouple, which was placed at the center of the reactor. This thermocouple was connected to digital thermometer readout. The furnace temperature was controlled to ±1°C by a controller. Effluent gas mixture of the reactor was quenched passing through a stainless steel heat exchanger so that the gas phase reaction is confined to the reactor only. The effluent temperature of the heat exchanger was measured with a Type T thermocouple, which was connected to the digital thermometer readout. While tap water was flowing in the outer pipe of the heat exchanger, the reactor outlet gas mixture passed through the inner pipe. The heat exchanger outlet was connected to an FTIR (Perkin–Elmer Spectrum One) with a heatable gas cell for on-line chemical analysis of the reactor exit stream. The gas cell temperature was kept constant at a temperature of 110°C in order to prevent condensation of BCl_3 in the cell. Considering the toxicity of BCl_3 gas and the flammability of H_2 gas, the furnace was placed under a stainless steel hood and the whole system was kept in a continuously vented room.

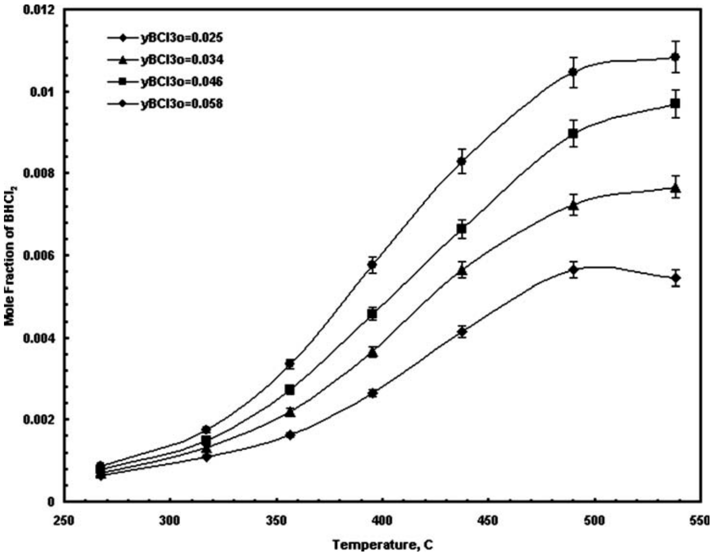

Figure 2. Effects of the initial mole fraction of BCl_3 (in hydrogen) and reactor temperature on the mole fraction of $BHCl_2$ at the reactor exit.

Experiments were carried out at atmospheric pressure and with a total volumetric flow rate of 200 cm^3/min and with different inlet gas compositions within the reactor temperature range of 300–600°C. Residence time was around 35 s and mixing time was expected to be at least an order of magnitude smaller than residence time. Two sets of experiments were performed in which either BCl_3 or H_2 were kept almost constant and the inlet concentration of the other reactant was varied. In these experiments, helium was used as an inert diluent to adjust the composition. BCl_3-H_2-He experiments were performed to observe the effects of hydrogen and boron trichloride concentrations on the reaction rate. Quantitative information about the compositions of the reactor effluent was obtained by calibrating the FTIR spectra for the reaction constituent gases according to the characteristic peak heights corresponding to a certain wavenumber. One for each component, relationships between mole fraction of the component and peak height at the certain wavenumber were established and mole fractions of the components in the effluent stream were found using these relationships. The instrument was calibrated using polystyrene sample. Some of the experiments were repeated to test the reproducibility of the results. The uncertainty of experiments determined by replicate runs was ±3.5%.

Results and Discussions

The analysis of the FTIR spectra revealed the existence of HCl and $BHCl_2$ in addition to hydrogen and boron trichloride, which are consistent with the previous studies.[6,11] IR absorption bands of boron trichloride and HCl were observed between 865 and 1055 cm^{-1} and 2500 and 3135 cm^{-1}, respectively. In addition of these peaks, the characteristic peaks of $BHCl_2$ were also obtained at 845–910, 1045–1135, and 2500–2690 cm^{-1}.[14]

The results of the experiments performed at different temperatures and inlet gas compositions showed that one independent reaction is sufficient to describe the reaction system investigated in this study.

$$BCl_3(g) + H_2(g) \rightarrow BHCl_2(g) + HCl(g)$$

Fractional conversion of boron trichloride to dichloroborane (x) was evaluated using the following mole fraction relations. Material balance around the reactor was checked by comparing the experimental values of the mole fractions with the mole fractions calculated from the Eqs. 1–3.

$$y_{BCl_3} = y_{BCl_{3i}}\ (1 - x) \quad (1)$$

$$y_{BHCl_2} = y_{BCl_{3i}} x \quad (2)$$

$$y_{HCl} = y_{BCl_{3i}} x \quad (3)$$

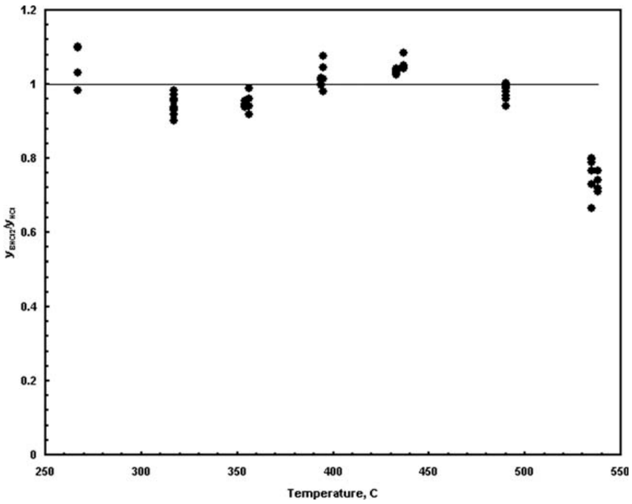

Figure 3. Temperature dependence of the ratio of the $BHCl_2$ mole fraction to the HCl mole fraction.

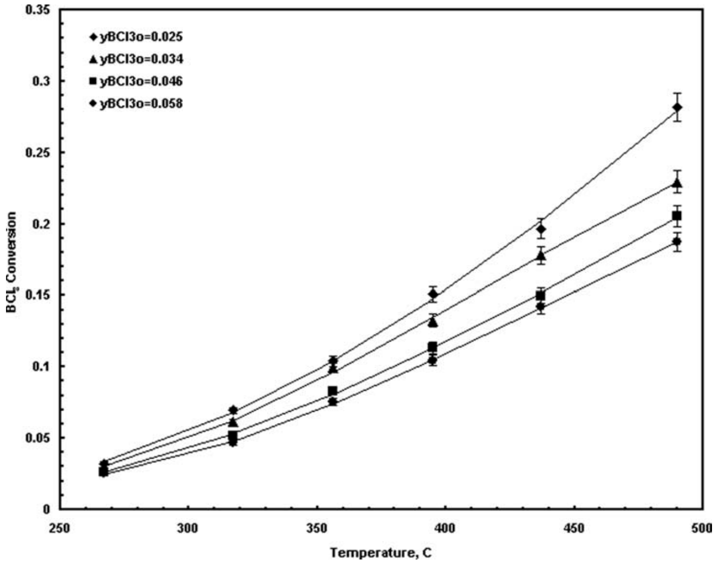

Figure 4. Effects of the initial mole fraction of BCl_3 (in hydrogen) and reactor temperature on the conversion of boron trichloride to dichloroborane.

Dichloroborane formation rate was determined from

$$R_{BHCl_2} = \frac{F_o y_{BCl_{3o}} x}{V} \tag{4}$$

Experimental results showed that the reactor system reached steady-state in a short time. Some fluctuations observed in the effluent gas composition at the initial times of the reaction were due to the change in reactor temperature during the heating or cooling process of the reactor (Supporting Information Figure S1). The effect of temperature on the mole fraction of $BHCl_2$ for different inlet BCl_3 mole fractions is illustrated in Figure 2. Formation of $BHCl_2$ started at a reactor temperature of around 170°C. It became measurable only over 250°C. As it is shown in this figure, the mole fraction of $BHCl_2$ increased with an increase in temperature up to 500°C. At temperatures above 500°C, change of the mole fraction of $BHCl_2$ was not significant. The variation of mole fraction ratio of $BHCl_2$ to HCl (in the product stream) with respect to temperature is shown in Figure 3. The mole fraction ratio of $BHCl_2$ to HCl remained around one up to the reactor temperature of 500°C. Over this temperature, it started to decrease to a value of 0.8 (at 535°C). A decreasing trend in this ratio is probably due to the boron formation reaction through CVD at high temperatures. Increase of the HCl mole fraction at temperatures over 500°C while the mole fraction of $BHCl_2$ was almost constant, is an evidence of the formation of boron

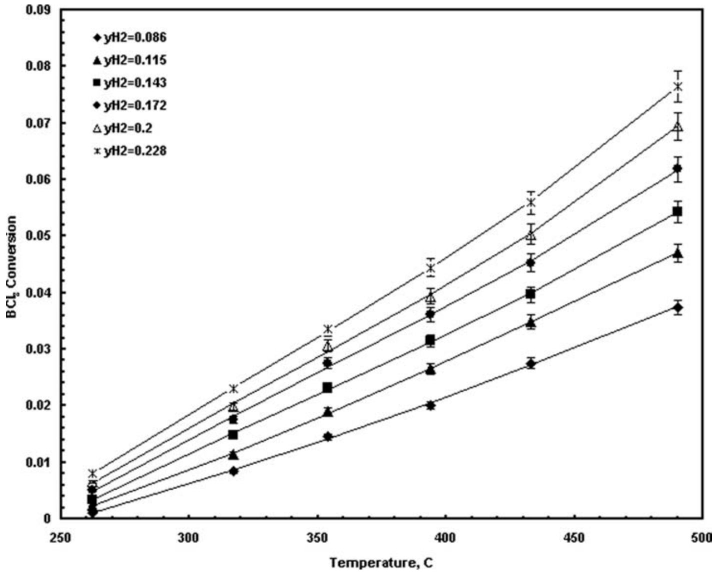

Figure 5. Change of the conversion of boron trichloride to dichloroborane with respect to the inlet mole fraction of hydrogen.

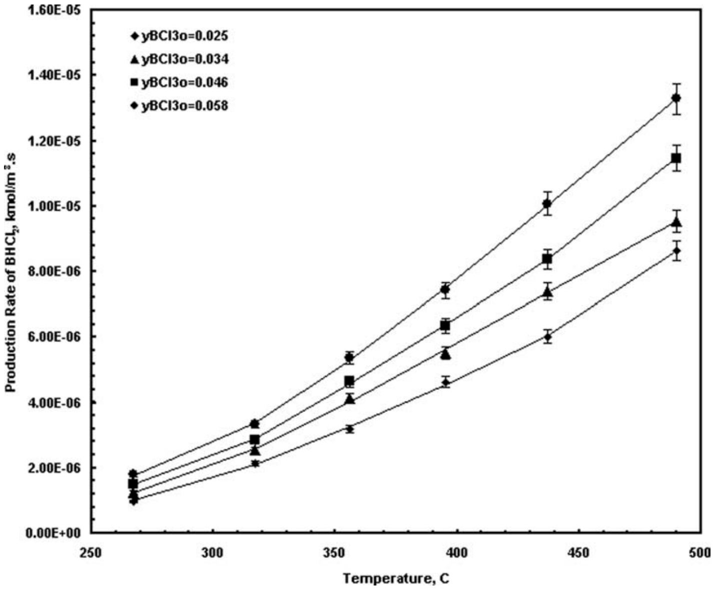

Figure 6. Change of the dichloroborane production rate with respect to the inlet mole fraction of boron trichloride.

together with $BHCl_2$. In other words, no deposition of boron was observed in the CSTR at temperatures lower than 500°C. The fractional conversion results of BCl_3 obtained at different initial mole fractions of BCl_3 and at different temperatures are given in Figure 4. It was observed that the conversion of BCl_3 increased with an increase in the temperature as expected. However, the fractional conversion of BCl_3 decreased with an increase in the inlet mole fraction of BCl_3.

In the BCl_3-H_2-He experiments performed by keeping the inlet BCl_3 mole fraction constant, the fractional conversion of BCl_3 to $BHCl_2$ showed an increasing trend with an increase in the inlet mole fraction of hydrogen (Figure 5). Variation of $BHCl_2$ production rate values, which were evaluated from Eq. 4, at different inlet BCl_3 and H_2 mole fractions are given in Figures 6 and 7, respectively.

To evaluate the rate expression for $BHCl_2$ formation from BCl_3 and H_2, two different approaches were used. In the first approach a simple power law model was assumed as follows

$$R_{\mathrm{BHCl_2}} = kC^{a}_{\mathrm{BCl_3}}C^{b}_{\mathrm{H_2}}$$

where $k = k_{\mathrm{o}}\exp\left(\frac{-E_{\mathrm{a}}}{RT}\right)$.

By using a nonlinear regression method, rate parameters of this model were obtained from the analysis of the dichloroborane formation reaction rate data. Sixty data points were used to determine the rate parameters. As a result of the regression analysis, the reaction orders with respect to the boron trichloride and hydrogen concentrations were found as 0.54 and 0.65, respectively, with a correlation coefficient of 0.993. The dependence of the reaction rate constant on temperature is shown in Figure 8.

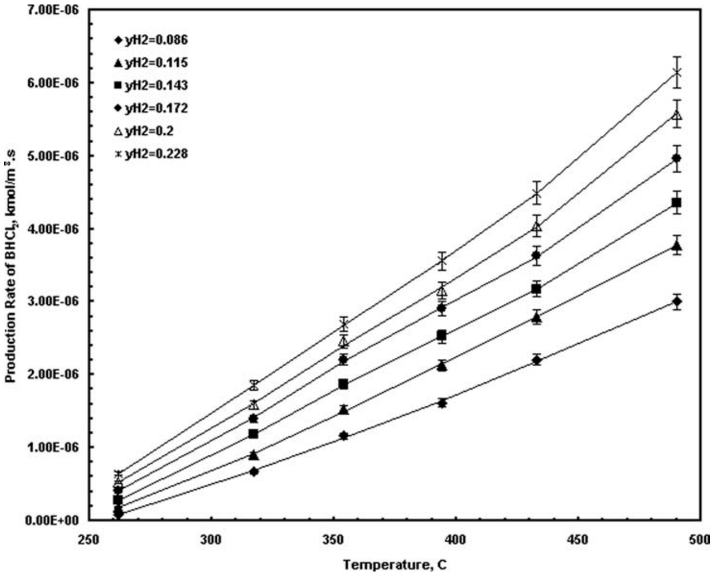

Figure 7. Effect of the inlet mole fraction of hydrogen on the dichloroborane production rate.

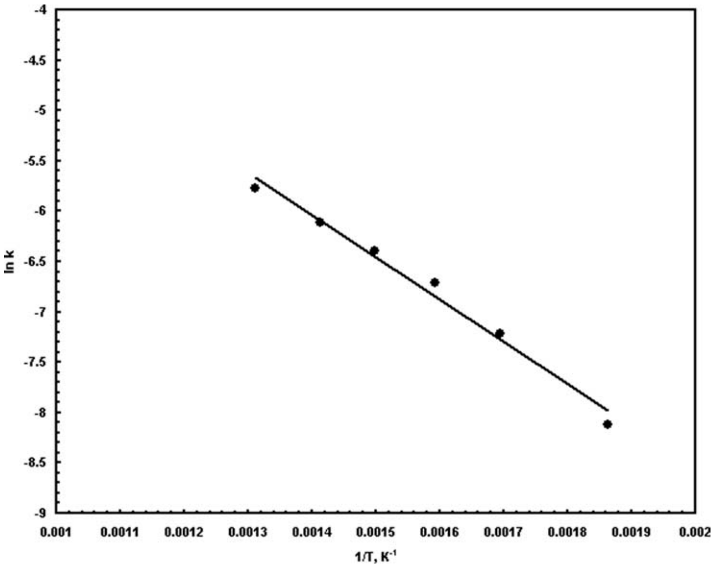

Figure 8. Temperature dependence of the reaction rate constant of the power law model.

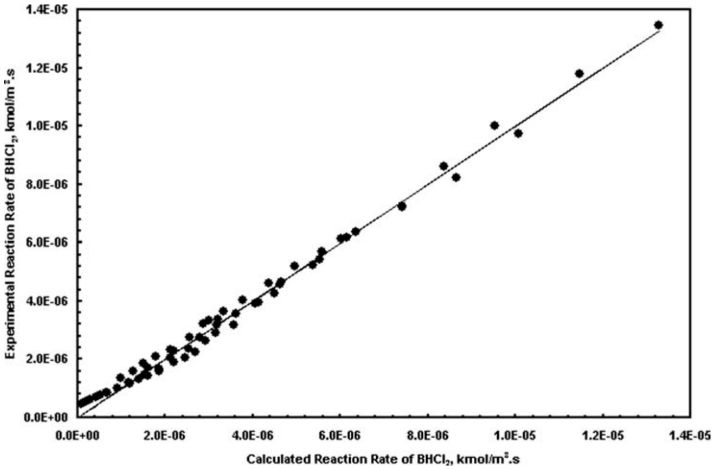

Figure 9. The experimental and calculated values of the dichloroborane's reaction rate for the power law model.

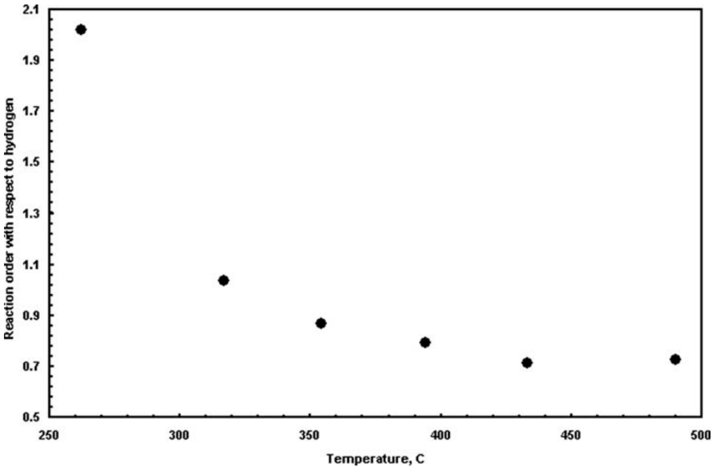

Figure 10. Effect of temperature on the reaction order with respect to hydrogen.

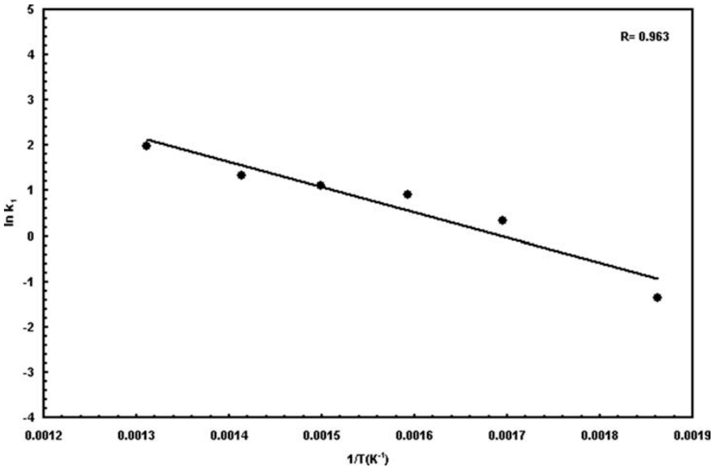

Figure 11. Temperature dependence of the first reaction rate constant of the second model.

The Arrhenius plot of these rate coefficients gave the activation energy of 30,230 J/mol and preexponential factor of 0.37 $(\text{kmol/m}^3)^{-0.19}\,\text{s}^{-1}$. Final rate expression found from this analysis is

$$R_{\text{BHCl}_2} = 0.37\exp\left(\frac{-30,230}{RT}\right)C_{\text{BCl}_3}^{0.54}C_{\text{H}_2}^{0.65}$$

As shown in Figure 9, experimental and calculated rate values from this model gave satisfactory results. However, some deviations were observed at low rate values, corresponding to a temperature of 262°C.

Data obtained in this work with almost constant BCl_3 and H_2 exit concentrations were also separately analyzed at each temperature to check if there was an effect of temperature on the observed reaction order. In fact, this analysis showed that reaction order with respect to hydrogen increased significantly at temperatures lower than 350°C (Figure 10). However, reaction order with respect to BCl_3 was almost constant at about 0.5 at each temperature. Considering these findings a new rate model was proposed as follows

$$R_{\text{BHCl}_2} = \frac{k_1 C_{\text{BCl}_3}^{0.5} C_{\text{H}_2}^{2}}{1 + k_2 C_{\text{H}_2}^{n}}$$

where $k_1 = k_{01}\exp\left(\frac{-E_{a1}}{RT}\right)$ and $k_2 = k_{02}\exp\left(\frac{-E_{a2}}{RT}\right)$.

Regression analysis of the data gave that for $n = 3/2$, this model gave very good agreement with the experimental data. The dependence of the reaction rate constants on temperature are shown in Figures 11 and 12. The Arrhenius plot of k_1 gave the activation energy of 55,500 J/mol and a preexponential factor of 172,819 $(\text{kmol/m}^3)^{-3/2}\,\text{s}^{-1}$. The activation energy and preexponential factor for the second rate coefficient k_2 were found as 23,100 J/mol and 379,648 $(\text{kmol/m}^3)^{-1/2}\,\text{s}^{-1}$, respectively.

Final rate expression derived from this model using all the data is as follows

$$R_{\text{BHCl}_2} = \frac{172,819\exp\left(-55,500/RT\right)C_{\text{BCl}_3}^{0.5}C_{\text{H}_2}^{2}}{1 + 379,648\exp\left(-23,100/RT\right)C_{\text{H}_2}^{3/2}}$$

Comparison of the experimental and the calculated values (Figure 13) from this model gave very good agreement, with

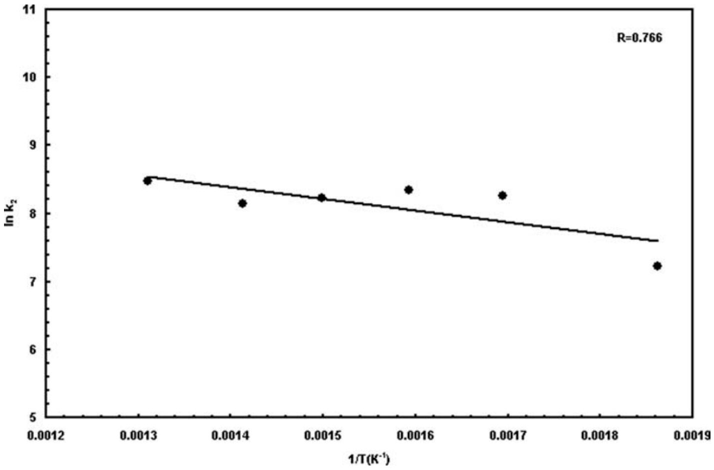

Figure 12. Temperature dependence of the second reaction rate constant of the second model.

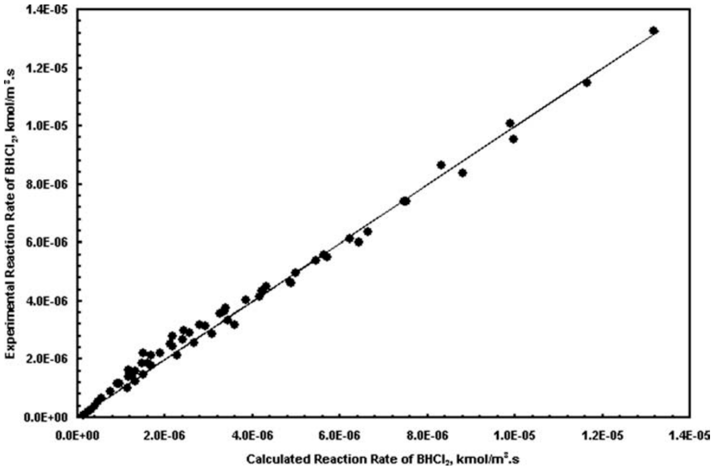

Figure 13. The experimental and calculated values of the dichloroborane's reaction rate for the second model.

a correlation coefficient of 0.995. Small deviations observed with the power law model at low temperatures (Figure 9) were not observed with this model. It was concluded that the analysis of the rate expression with the experimental data gave good agreement.

Conclusions

In this study, detailed kinetic information about the gas phase reaction between boron trichloride and hydrogen was obtained in the CSTR type of reactor. Such data are essential for the design of a CVD reactor for boron fibre production. The dichloroborane formation reaction was found to start at a reactor temperature of around 170°C and boron formation reaction started above the reactor temperature of 500°C. It was observed that there is only one reaction taking place in the gas phase below 500°C which is the dichloroborane formation reaction. While reaction order with respect to hydrogen increased significantly at temperatures lower than 350°C, reaction order with respect to BCl_3 was almost constant at about 0.5 at each temperature. The rate expression derived for this gas phase reaction could be used in the design of CVD reactors for boron fibre and boron thin film production.

Notation

a = reaction order with respect to the concentration of boron trichloride
b = reaction order with respect to the concentration of hydrogen
C_i = concentration of component i, kmol/m^3
E_a = activation energy of the reaction, J/mol
F_o = initial molar flow rate of gas mixture, kmol s^{-1}
k = reaction rate constant, (kmol/m^3)$^{1-n}$ s^{-1}
R_i = reaction rate of component i, kmol/(m^3 s)
R = ideal gas constant, J/mol K
T = temperature, K
V = volume of the reactor, m^3
y_i = mole fraction of component i in the product stream
y_{io} = mole fraction of component i in the reactant stream
x = conversion of boron trichloride to dichloroborane

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