



Modeling the hydrochlorination reaction in a laboratory-scale fluidized bed reactor



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ABSTRACT

In the manufacturing process of high purity, electronics-grade silicon, the hydrochlorination reaction step for converting silicon tetrachloride (STC) to trichlorosilane (TCS) is usually carried out in a fluidized bed reactor. However, the design and operation of industrial-scale fluidized bed reactors for the conversion of STC to TCS is currently based on ad hoc rules of thumb and operator experience rather than on reaction engineering principles. In this paper, a fluidized bed model was developed by using the Kunii–Levenspiel fluidization framework. The predictive capabilities of this model were tested on laboratory-scale experimental data from the literature. It is shown that the modified Kunii–Levenspiel model accurately predicts the no catalyst addition and copper catalyst addition experiments of the hydrochlorination fluidized bed with an average percent difference of less than 6%. By making a suitable adjustment to catalytically active iron content, the model prediction is in excellent agreement with experimental data with hydrochloric acid in the feed stream. The modified Kunii–Levenspiel model is well suited for use in scale-up calculations for an industrial reactor as all the parameters are physically reasonable and can be predicted for larger reactors.

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1. Introduction

Silicon is the second-most abundant element on the Earth's crust. However, it rarely occurs in pure form and most silicon is used commercially with little or no processing in the building industry (clays, silica sand and stone, Portland cement) and the ceramics industry. Metallurgical-grade silicon (98% pure) is also used in steel refining and aluminum-casting. However, the electronics industry requires a very highly purified form of silicon and the most common approach to purifying silicon involves the conversion of metallurgical-grade silicon into volatile liquids, such as trichlorosilane (TCS) and silicon tetrachloride (STC). TCS is separated by distillation and the byproduct, STC, can be converted to TCS by a hydrochlorination process. Gaseous TCS is blown over the surface of a pre-existing pure silicon seed rod heated to a high temperature and high-purity silicon crystallites are grown directly on the surface via chemical vapor deposition [1].

Mui and Seyferth [1] proposed that the conversion of STC to TCS is a two-step process as shown below:



The hydrochlorination reaction step for converting STC to TCS is usually carried out in a fluidized bed reactor. The use of a fluidized bed reactor is advantageous due to the large surface area available for reaction and the removal of inert solids by carry-over. However, the design and operation of industrial-scale fluidized bed reactors for the conversion of STC to TCS is currently based on ad hoc rules of thumb and operator experience rather than on reaction engineering principles. Developing a scalable model from the laboratory fluidized bed is particularly important because of the potential for inefficiencies in larger reactors [2]. In this paper, a fluidized bed model is developed by using the Kunii–Levenspiel fluidization framework [2]. The predictive capabilities of this model are tested on laboratory-scale experimental data from the literature.

Experimental results from Cygon [3] and Sill et al. [4] were used to test the model developed in this paper. These are the only published results suitable for testing the hydrochlorination model. The quality of the results is very good and the tests judiciously spanned the relevant industrial reaction conditions. In addition, many of the results intentionally did not reach equilibrium and are therefore useful for testing the hydrodynamic aspects of a fluidized bed hydrochlorination reaction

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model. These experiments were conducted in a laboratory-scale fluidized bed reactor to study the conversion of STC to TCS. The reactor was glass-lined to preclude possible catalytic effects of the wall. All experiments were carried out at atmospheric pressure. The laboratory scale reactor had a 5 cm internal diameter. Cygon and Sill varied important reaction parameters such as temperature, superficial feed velocity, hydrogen/STC ratio, bed height (through initial metallurgical silicon charge), copper catalyst addition, and the addition of hydrochloric acid to the feed stream. Superficial velocity was varied from 4 to 12 cm/s. Temperature ranged between 500 and 600 °C. Molar ratio of hydrogen to STC was varied from 0.67 to 4. HCl was added from 1.7 to 6% on a total volume basis. Most experiments were executed with a 400 g charge of metallurgical silicon resulting in a static bed height of 16.5 cm. Some tests decreased the metallurgical silicon to 100 g resulting in a static bed height of 4.12 cm. A majority of experiments utilized metallurgical silicon with a mean Sauter diameter of 182 μm although some tests used 278 μm particles. Pure liquid STC was sent to an evaporator and thereafter mixed with hydrogen. The short-term experiments of interest for this work used metallurgical silicon, which was reacted for less than 10 h, representing about 10% silicon conversion.

Lehnen's [5] analytical chemistry work provided a foundation for the kinetic data developed by Becker [7]. Lehnen showed that initially, metallurgical silicon is coated with a silicon dioxide (SiO₂) layer that inhibits reaction. The hydrochlorination reaction without catalyst addition occurred due to iron impurities in the silicon. When the reactor was heated, aluminum impurities were rapidly discharged as aluminum trichloride (AlCl₃) thereby exposing a greater surface area of catalytically active iron. Sill [6] reported that large areas in the surface on the silicon did not react without catalyst addition. Sill [6] also reported that with copper catalyst the reaction proceeded at the surface in a structured orientation. He reported finding reaction sites typically found in the iron catalyzed reaction that produced holes in the silicon; however, the surface reaction by copper dominated. Becker [7] suggested that the kinetic mechanism of the hydrochlorination reaction was a result of catalytically active iron inherent to metallurgical silicon along with a parallel reaction with copper when it is added as a catalyst. Becker [7] developed separate kinetic models for the iron reaction and the copper catalyzed reaction. He tested several kinetic models, and for each case chose a kinetic rate expression based on power laws as this provided the least error when compared to Lehnen's [5] experimentation.

Becker [7] proposed the following kinetic equation for the hydrochlorination reaction as catalyzed by the iron impurities inherent to the silicon.

$$r_{\text{Fe}_x\text{Si}_y} = a_{\text{Fe}} k_{\text{Fe}_x\text{Si}_y} \frac{p_{\text{SiCl}_4}^{x_{\text{SiCl}_4, \text{Fe}_x\text{Si}_y}} p_{\text{H}_2}^{x_{\text{H}_2, \text{Fe}_x\text{Si}_y}}}{p_{\text{SiHCl}_3}^{x_{\text{SiHCl}_3, \text{Fe}_x\text{Si}_y}}} \left(1 - \frac{Q_p}{K_p}\right) \quad (4)$$

Because the specific activity of the metallurgical silicon was unknown, the initial product of the specific activity and the reaction rate constant pre-exponential factor was interpreted as a free parameter. In this factor, the activation energy and the exponential powers were chosen to minimize the sum squared error of experimentation. The values of the resulting parameters are shown in Table 1.

Table 1
Parameters of the iron catalyzed kinetic equation.

$a_{\text{Fe}} k_{\text{Fe}_x\text{Si}_y}$ mol ¹ kgcat ⁻¹ s ⁻¹ Pa ⁻¹⁰⁰³	$E_{A, \text{Fe}_x\text{Si}_y}$ J/mol	$x_{\text{SiCl}_4, \text{Fe}_x\text{Si}_y}$	$x_{\text{H}_2, \text{Fe}_x\text{Si}_y}$	$x_{\text{SiHCl}_3, \text{Fe}_x\text{Si}_y}$
1.598*10 ⁻¹	120,073	2.521	0.501	2.019

The power law kinetics indicates that the reaction is based on the chemisorption of the reactant species. The thermodynamic equilibrium constant K_p was derived from the work of Mui [8].

$$K_p = 0.329 \exp\left(\frac{-36,200}{RT}\right) \quad (5)$$

The reaction quotient is defined by Eq. (6).

$$Q_p = \frac{p_{\text{SiHCl}_3}^4 p_{\text{atm}}}{p_{\text{SiCl}_4}^3 p_{\text{H}_2}^2} \quad (6)$$

Becker [7] theorized that the copper catalyzed hydrochlorination reaction occurs in parallel with the iron catalyzed reaction. The best kinetic model for this reaction was also a power law with inhibition.

$$r_{\text{Cu}_x\text{Si}_y} = a_{\text{Cu}} k_{\text{Cu}_x\text{Si}_y} \frac{p_{\text{SiCl}_4}^{x_{\text{SiCl}_4, \text{Cu}_x\text{Si}_y}} p_{\text{H}_2}^{x_{\text{H}_2, \text{Cu}_x\text{Si}_y}}}{p_{\text{SiHCl}_3}^{x_{\text{SiHCl}_3, \text{Cu}_x\text{Si}_y}}} \left(1 - \frac{Q_p}{K_p}\right) \quad (7)$$

Again, the specific activity and reaction rate constant, the activation energy and the exponential factors were taken as free parameters and adjusted to minimize the sum of square error between experimental data and the kinetic model. The resulting parameters are shown in Table 2.

These reaction mechanisms are incorporated in a fluidized-bed model in the next section.

2. Model development

Levenspiel developed a hydrodynamic model for fluidized bed reactors with fine fluidized particles [9]. In this model, the bubbles rise faster than the emulsion and are surrounded by a cloud of particles that move at the same rate as the bubble. In addition, a wake of solids is dragged behind the bubble. The process gas in the bubble forms a vortex and is segregated from the gas in the cloud-wake and emulsion phase. Within this gas are sparsely distributed solids where some reaction occurs. A modification of this model was developed for larger particles (Geldart A and Geldart AB classification) by Kunii and Levenspiel [2]. In this model, the bubble and a cloud of solids around the bubble rise up rapidly through an emulsion that is at minimum fluidization conditions. Since the cloud volume is small, gas flow through the cloud is ignored. In addition, the emulsion phase is considered to be stagnant. The model is composed of three phases: the bubble containing a small amount of entrained solids, the cloud-wake of solids surrounding and rising with the bubble, and the emulsion phase with solids at minimum fluidization conditions. These assumptions are valid when the superficial velocity over the minimum fluidization velocity is much greater than 1 [2].

$$\frac{u_0}{u_{mf}} \gg 1 \quad (8)$$

The Kunii–Levenspiel model is combined with the reaction kinetics to give the following equation for a given reactant, intermediate, byproduct, or product.

$$\left(\text{overall disappearance in bubble}\right) = \left(\text{reaction in bubble}\right) + \left(\text{transfer to cloud-wake}\right) \quad (9)$$

Table 2
Parameters of the copper catalyzed kinetic equation.

$a_{\text{Cu}} k_{\text{Cu}_x\text{Si}_y}$ mol ¹ kgcat ⁻¹ s ⁻¹ Pa ⁻¹⁰⁸⁶	$E_{A, \text{Cu}_x\text{Si}_y}$ J/mol	$x_{\text{SiCl}_4, \text{Cu}_x\text{Si}_y}$	$x_{\text{H}_2, \text{Cu}_x\text{Si}_y}$	$x_{\text{SiHCl}_3, \text{Cu}_x\text{Si}_y}$
1.3878*10 ⁻²	109,557	2.532	0.629	2.075

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