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Conversion of hydrogen chloride to chlorine by catalytic oxidation in a two-zone circulating fluidized bed reactor

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ABSTRACT

A two-zone circulating fluidized bed reactor comprising an oxychlorination zone and a chlorination zone significantly improved the conversion of HCl to Cl_2. A supported catalyst for the process composed of 5% of copper, and promoters K in a molar ratio of K to Cu of one and 2.5% CeCl was highly active and stable. The optimal operation temperatures are 390–400 °C in the oxychlorination zone and 200–240 °C in the chlorination zone. A higher conversion of HCl can be obtained with a lower WHSV of HCl and a lower HCl/O_2 molar ratio, but the height of the reactor must be high enough.

1. Introduction

Chlorine is the primary raw material for a large number of chloride products. It is mainly produced by the electrolysis of NaCl, with the coproduct of caustic soda. Chlorine and caustic soda have different use outlets and it is part of the skill of chloro-alkali marketers to balance the demand for the two products. Nowadays, the industry suffers from chlorine shortage and caustic soda glut, due to the strong chlorine demand from the world growth in PVC demand of 5.5% pa.

In many of the chemical processes, chlorine is used but it does not appear in the product because it is employed as an intermediate in the reaction. For example, the production of toluene diisocynate (TDI) requires the use of the chorine derivative phosgene, but none of the chlorine appears in the TDI molecule, and instead it has to be removed as the by-product hydrogen chloride (HCl). The HCl by-product must be disposed of in an environmentally safe manner. Currently, the primary method of HCl disposal is by neutralization, which is costly. Increasingly stringent regulations, in addition, limit the shipment of this potentially hazardous waste. As a result, there is a strong incentive worldwide to develop an efficient process for the *in situ* recovery of Cl_2 from HCl waste by-product so that Cl_2 can be recycled and reused within the process itself.

Many literature reports have described processes for producing Cl_2 from by-product HCl. These include the electrolysis of HCl to produce Cl_2 and H_2 [1,2], direct oxidation using inorganic agents [3,6], and catalytic oxidation by air or O_2 [4,5]. For the electrolysis, equipment investment and energy consumption costs are very high, and the electrolyte/electrode materials are sensitive to impurities commonly found in process streams associated with waste HCl. In the direct oxidation process, the conversion of HCl is not high enough and more waste must be disposed [3,6]. The catalytic oxidation process of HCl, called the Deacon process, is one of the earliest catalytic processes, dating back to the late 1800s [7]. In this, HCl is oxidized by oxygen or air in the presence of a $CuCl_2$ catalyst. The chemical reactions are as follow [8]:

$$\text{Oxidation}: \ CuO + 2HCl \rightleftharpoons CuCl_2 + H_2O \qquad \Delta H_1 = -28.8\,\text{kcal/mol} \tag{1}$$

$$\text{Chlorination}: \ CuCl_2 + 0.5O_2 \rightleftharpoons CuO + Cl_2 \qquad \Delta H_2 = 15.0\,\text{kcal/mol} \tag{2}$$

Since the above reactions are reversible, the equilibrium conversion of HCl is usually below 80%, which is unacceptable for industrial use.

From an analysis of the above reactions, it is known that a high HCl conversion can be achieved if the above two reactions are carried out at different reaction temperatures with oxidation at a high temperature and chlorination at a low temperature, respectively. Based on the reaction kinetics and thermochemical studies, Benson et al. [9] have developed a dual interconnected fluidized bed reactor system for the Deacon process.

During operation, a stream of HCl in O_2 and N_2 is continuously supplied to one of the fluidized bed reactors [13], the “oxidizer”,

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working in the temperature range of 340–400 °C. In the oxidizer, both oxidation and chlorination take place, and HCl is converted to chlorine and water vapor. The exit stream from the oxidizer is then fed to the second reactor, the "chlorinator", operating in the temperature range of 180–200 °C where any HCl left unreacted from the oxidizer reacts with the catalyst present to give a HCl-free chlorinator exit stream. The catalyst in the chlorinator, after reacting with the HCl, is subsequently recirculated into the oxidizer, where it is "regenerated" in the presence of oxygen. However, based on our research experience in fluidization studies of three decades, the comment can be made that it is difficult to operate the dual interconnected fluidized bed reactor because the pressure in the chlorinator is higher than that in the oxidizer and it is difficult to recirculate the catalyst in the chlorinator into the oxidizer.

Using the above analysis, we had proposed a new two-zone circulating fluidized bed reactor for the Deacon process [10]. Here, we report further experimental studies that are relevant to the scale-up. The study aimed to offer the opportunity for the chloro-alkali industry to increase the degree of chlorine recycle sufficiently to eliminate the looming chlorine shortage.

2. Experimental

The catalyst for the experiments was prepared by the impregnation of γ-Al_2O_3 which was obtained from Shandong Zibo Aluminium Factory (specific surface area is 200 m^2/g, pore volume is 0.137 cm^3/g, average particle diameter is 50 μm). The main active component was $CuCl_2$ and the promoters were KCl and CeCl. HCl (semiconductor grade, purity >99.99%) and oxygen (purity >99.5%) were used for the reaction. Nitrogen (purity >99.5%) was used as an inert gas.

A bench scale, two-zone circulating fluidized bed reactor system was designed and built to study the catalytic oxidation of HCl to Cl_2. The experimental setup is shown in Fig. 1. The reactor was separated into two zones by a tubiform distributor in the middle of the riser. The tubiform distributor consisted of some small pipes. Gas flow rate in the pipes was high enough to make sure that the catalyst particles can only flow from the bottom section to top section, and prevent the catalyst from the top section mixing with the catalyst from the bottom section. The lower zone with a height of 800 mm was the oxychlorinator, where the endothermic oxidation (1) and the exothermic chlorination (2) took place simultaneously at a high temperature. This was the conventional Deacon process, namely the chlorination (2) provides the reaction heat for the oxidation (1). The upper zone with a height of 600 mm was the chlorinator, where only the exothermic chlorination (1) took place at a low temperature. The reactor was made of stainless steel. The riser was 50 mm in inner diameter (ID) and the catalyst downcomer was 40 mm ID.

The reactor temperature was controlled by CKW-1100 temperature controllers. Each controller used a K type (nickel–chromel) thermocouple for the accurate measurement of the temperature of the fluidized bed reactor. To measure the temperature in the different parts of the reactor, 7 thermocouples were installed. Before use, each thermocouple was calibrated. The temperature controllers were connected to heaters made with nickel–chromium alloy heating wire insulated with ceramic beads and glass wool. These heaters were effective in maintaining accurate temperatures. There was a cooler in the chlorinator to reduce the temperature. The whole reactor except the chlorinator was heated or insulated so that no water can condense in it.

The reactor system was equipped with a reactant gas handling and delivery system, which accurately controlled the composition and flow rates of the feed gases. The gases were delivered from gas cylinders with two-stage gas regulators. The regulator for the HCl stream was corrosion resistant. The gases were passed through calibrated glass rotameters fitted with a stainless steel float and polypropylene seals and through a series of three-way Pyrex glass valves for mixing and directing the gases to the reactor section. The tubing and connections used to transport the reactant gases were made of Teflon to resist damage from the corrosive gas HCl.

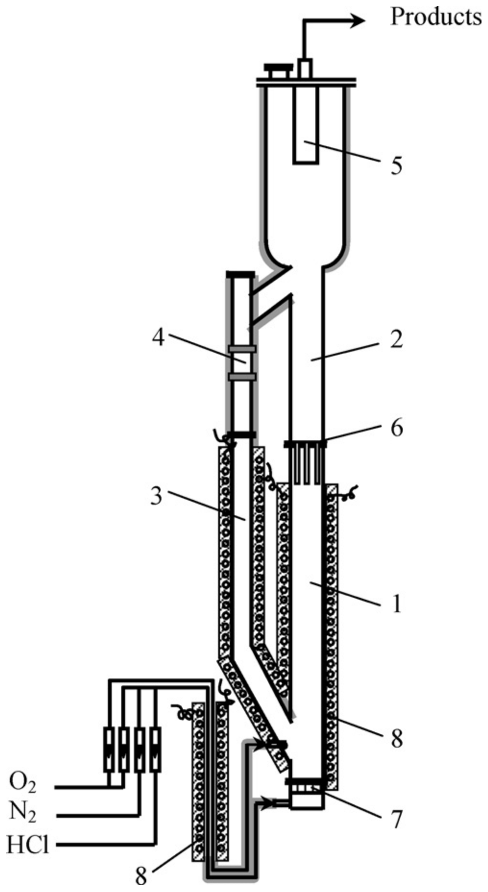

Fig. 1. Experimental setup of the HCl catalytic oxidization process. 1. Oxychlorinator, 2. Chlorinator, 3. Downcomer, 4. Sight glass, 5. Filter, 6. Tubiform distributor, 7. Sintered plate distributor, 8. Heater.

The experiment was conducted as follows: before the experiments, about 2 kg catalyst was fed into the reactor. The fresh gas (HCl in O_2 or air) was fed into the oxychlorinator through the sintered plate distributor at the bottom of the reactor, and nitrogen was fed to enhance fluidization and catalyst circulation. Oxychlorination was operated at elevated temperatures (340–400 °C) and the HCl was partially converted to Cl_2 producing an exit gas stream consisting of HCl, Cl_2, unreacted O_2, N_2, and water vapor. This "exit" gas was then flowed upwards though the tubiform distributor into the chlorinator, which was operated at lower temperatures (180–250 °C). In the chlorinator, unreacted HCl reacted further, with the catalyst, producing a gaseous product stream containing less HCl. The gas and catalyst particles were separated at the top of the reactor. The product stream was then sent to a gas absorption and analysis system to evaluate the reactor performance, while the catalyst particles were returned to the oxychlorinator through the downcomer.

In order to understand the effect of reactor size on the process, experiments in bench scale and pilot plant reactors were carried out. For the bench scale reactor, the riser was 50 mm in inner diameter (ID) and the catalyst downcomer was 40 mm ID, the lower zone height of the riser was 800 mm and the upper zone height was 600 mm; for the pilot scale reactor, the riser was 140 mm in inner diameter (ID) and the catalyst downcomer was 80 mm ID, the lower zone height of the riser was 2400 mm and the upper zone height