



Ethene oxychlorination over $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst in micro- and millistructured reactors

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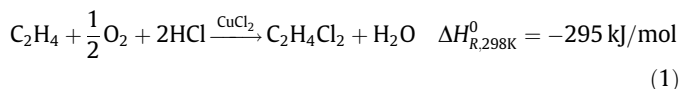
ABSTRACT

Oxychlorination of ethene was performed over $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst in a microreactor (460 μm in diameter) and for comparison in a millireactor (1 cm in diameter). A copper-modified catalyst was prepared by a conventional evaporation–impregnation method without any promoters (e.g., K, Na, La) using copper (II) chloride as a precursor. The catalyst was characterized by nitrogen physisorption, Fourier transform infrared spectroscopy using pyridine, temperature-programmed desorption of CO_2 , scanning electron microscopy, energy-dispersive X-ray microanalysis, and transmission electron microscopy. Different reactor types led to notable differences in catalytic performance at the same partial pressures in terms of both activity and selectivity. A higher reaction rate was achieved in the microreactor, which was 4.5 times faster. The activity decline and different selectivity to the desired product are explained by a change in the oxychlorination mechanism due to a different ratio of reagents in the mixture during the reaction.

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1. Introduction

Polyvinyl chloride (PVC), the second most widely consumed plastic, is a material generally used in pipes, cables, and other construction applications. The production of PVC in China alone was 15.3 Mton in 2013 [1]. Almost the entire global production of PVC is based on the polymerization of vinyl chloride (VC) [2], which is obtained by cracking $\text{C}_2\text{H}_4\text{Cl}_2$, made via oxychlorination of ethene over CuCl_2 catalyst:



A detailed knowledge of the oxychlorination process and the reliability of the experimentally determined kinetic parameters is important for successful design of industrial reactors and manufacturing technology. Therefore, an accurate collection of experimental data and evaluation of kinetic parameters on the laboratory scale with reliable experimental equipment is necessary. Traditionally, the kinetics of catalytic gas-phase reactions is determined

in fixed-bed reactors with catalyst powders. Recently, interest in microreactors has grown because their specific properties are suitable for kinetic studies. Among the most important properties for a study of heterogeneously catalyzed reactions are, for example, a high internal surface-to-reaction-volume ratio, a thin catalyst layer, very precise control of operation conditions, a controlled flow of the reaction mixture, low consumption of chemicals, rapid catalyst testing, and safe operation of reactions even under explosive conditions [3,4].

With characteristic reactor size decreasing to less than 1 mm and especially below 100 μm , the influence of gravity is gradually eliminated due to the increasing influence of interfacial tension, wettability, and surface roughness [5]. By reducing the linear dimensions of the device, the effect of the convective movement of a reaction mixture is significantly diminished and diffusion becomes the dominant transport process. The distance of molecular diffusion is typically short, and thus the driving forces of the transport phenomena and the diffusion flow per unit volume or area are significantly higher. Acceleration of diffusion phenomena allows kinetic studies of very rapid reactions. The specific surface area of a microreactor channel often exceeds the specific surface area of standard devices by more than 50 times. A very high ratio of the internal surface area to the reaction volume of a microreactor (up to 5000–30,000 m^2/m^3) leads to significantly higher mass

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transfer coefficients (up to 10 s^{-1}) and heat transfer coefficients (up to $25,000\text{ W m}^{-2}\text{ K}^{-1}$) [6].

As a result, strongly exothermic reactions with the necessity of efficiently removing the reaction heat, eliminating local overheating, and operating under isothermal conditions are often investigated in microreactors. For instance, high selectivities can be achieved for substances that are not thermodynamically too stable, using a microreactor for multistage processes such as the hydrogenation of polyenes [7].

The mechanism of ethene oxychlorination over classical CuCl_2 -based catalysts has been studied using in situ and operando characterization by X-ray absorption fine structure (XAFS), X-ray absorption near-edge structure (XANES), and infrared (IR) and electron paramagnetic resonance (EPR) spectroscopy, as well as density functional theory calculations [2,8–11]. It is almost generally accepted that the mechanism of oxychlorination involves a three-step redox process: (i) reduction of CuCl_2 to CuCl , (ii) oxidation of CuCl to give an oxychloride, and (iii) closure of the catalytic circle by rechlorination with HCl , restoring the original CuCl_2 [8,10,12]. The activation energies are respectively 84 and 201 kJ/mol for the fly-ash-mediated oxychlorination and oxidation of ethylene [13].

The competition between oxidation and chlorination processes results in varying selectivities, depending on the conditions (particularly the temperature and the reactant partial pressures), which influence the catalyst surface composition [8]. The coverage and the composition of the catalyst surface are crucial for the overall behavior. All dopants contribute with varied efficiency to an increase of the fraction of active copper species, reaching a value of almost 100% in the case of MgCl_2 or LaCl_3 additives [8,14]. This observation is in line with the work of Rout et al. [15], who stated that maintaining a high Cu^{2+} concentration is the key to high activity, selectivity, and stability of CuCl_2 oxychlorination catalysts. In contrast, the penetration of iron into the catalyst due to erosion in industrial reactor walls leads to an increase of the yield of the total oxidation products and a decrease in the oxychlorination rate [16].

There are different opinions on the role of copper-containing surface sites in the main and side reactions of the overall ethene oxychlorination process [15,16]. All chloroorganic byproducts except ethyl chloride result from secondary 1,2-dichloroethane transformations, with dichloroethane dehydrochlorination and partial oxidation being the primary reactions in such transformations. Vinyl chloride and chloroethanol are converted further to 1,1,2-trichloroethane, trichloroacetaldehyde, trichloromethane, tetrachloromethane, dichloroethene, CO_2 , and CO [17]. Ethyl chloride is formed by ethene hydrochlorination. This reaction follows first-order kinetics with respect to ethene and hydrogen chloride and is inhibited by steam [12,17].

All chemical reactions included in the mechanism of ethene oxychlorination were considered to be irreversible, except for ethene hydrochlorination to ethyl chloride [12]. It should be noted that the equilibrium of the last reaction depends on the partial pressure of ethyl chloride. The work of Carmello et al. [11] demonstrated that neat alumina is the most active catalyst for dehydrochlorination. Addition of 1 wt% copper resulted in an evident decrease of ethyl chloride conversion to ethene. Chlorination of alumina with HCl only partially hinders the dehydrochlorination occurring through ethoxy groups [11,12].

This study of oxychlorination in micro- and millichannel reactors represents a further effort to elucidate the factors influencing the catalytic behavior of the system. The catalyst was devoid of any promoters, making elucidation of the effect of the support on activity, stability, and selectivity more apparent.

2. Experimental

2.1. Catalyst synthesis

Before the synthesis of the copper-containing catalyst, γ -alumina ($\gamma\text{-Al}_2\text{O}_3$ VGL-25, UOP Inc.) to be used as a support was crushed and sieved into a fraction $<32\text{ }\mu\text{m}$ in a vibratory micro mill (Fritsch). A copper-modified catalyst was prepared by a conventional evaporation-impregnation method without promoters (e.g., K, Na, La). Copper(II) chloride dihydrate ($\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, p.a., Honeywell) was used as a copper chloride precursor. The catalyst synthesis was carried out in a stirred bath containing 250 mL of 0.02 M aqueous solution of the metal precursor and 5 g of the catalyst support. The solution was rotated for 24 h at $60\text{ }^\circ\text{C}$, and subsequently water was evaporated at $40\text{ }^\circ\text{C}$ under vacuum. The copper chloride catalyst with a nominal loading of 5 wt% was dried in an oven at $100\text{ }^\circ\text{C}$ for 7 h and calcined in a step calcination procedure: initial temperature $250\text{ }^\circ\text{C}$ (held for 50 min) increased at $4\text{ }^\circ\text{C}/\text{min}$ to $450\text{ }^\circ\text{C}$ and held at the final temperature for 3 h.

The same powder catalyst was used in both reactors, as pellets ($250\text{--}500\text{ }\mu\text{m}$) in a millireactor and as coated platelets in a microreactor. The suspension method for microreactor platelet coating was based on a previously published procedure [18]. Prior to the coating, the platelets were cleaned with soap and distilled water, thereafter cleaned with acetone, and finally flushed with distilled water. The platelets were calcined in air to create an oxide layer on the platelets, which provided corrosion protection and enhanced the adhesion of the coating. The calcination procedure was started at an initial temperature of $350\text{ }^\circ\text{C}$, held for 85 min, and then increased at $4\text{ }^\circ\text{C}/\text{min}$ to $750\text{ }^\circ\text{C}$ with a holding time of 2 h at the final temperature.

The pretreated platelets were coated with the catalyst material, using the slurry deposition method. The slurry was prepared by adding water to a copper-modified catalyst on an alumina support with a particle size less than $32\text{ }\mu\text{m}$. The solid content in the slurry was 14 wt% $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$. The pH of the slurry was set to 8.9 by adding an ammonium hydroxide solution (25% for analysis, Merck KGaA). The slurry was stirred for 4 h at $40\text{ }^\circ\text{C}$ and for 24 h at room temperature. Only fresh slurries were used for coating.

The slurry (10 μL) was deposited into nine channels on each platelet with a Finnpiette. The catalyst on the platelet surface outside the channels was removed using a plastic spoon. The coated platelets were dried in a refrigerator to ensure slow drying and coating uniformity. Finally, the coated platelets were calcined in air at $250\text{ }^\circ\text{C}$ for 50 min and $400\text{ }^\circ\text{C}$ for 3 h, applying a heating rate of $3\text{ }^\circ\text{C}/\text{min}$. The mass of the catalyst was determined by weighing 10 platelets before and after the coating procedure. The amount of the catalyst placed on one platelet was found to be $1.485 \pm 0.055\text{ mg}$ and the average layer thickness determined by SEM was $38\text{ }\mu\text{m}$. The stability of the coating was tested by using the plates in an ultrasonic bath for 4 h.

2.2. Catalyst characterization

The specific surface area and the pore volume of the support and the copper chloride-containing catalyst were determined by nitrogen physisorption by a Sorptometer 1900 (Carlo Erba Instruments). The numbers of Lewis and Brønsted acid sites on the catalyst were quantified by Fourier transform infrared spectroscopy (FTIR) using pyridine ($\geq 99.5\%$) as the probe molecule (ATI Mattson FTIR Infinity Series). The basicity was studied by performing temperature-programmed desorption of CO_2 (CO_2 TPD, Micromeritics Instrument AutoChem 290) using a conventional flow-through reactor with CO_2 as a probe molecule. A scanning electron microscope (SEM; Zeiss Leo Gemini 1530) was used for determination of the crystal morphology. The copper and chlorine

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