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Kinetics of ethanol hydrochlorination over γ -Al₂O₃ in a microstructured reactor



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HIGHLIGHTS

- Ethyl chloride synthesis was successfully performed in two microreactors.
- Thermodynamic analysis of equilibrium constants and compositions.
- A Langmuir–Hinshelwood-type kinetic model was developed.
- The formation of all side-products was modeled.
- Influence of HCl on ethanol dehydration reactions was highlighted.

ARTICLE INFO

Article history:

Received 30 June 2014

Received in revised form

29 April 2015

Accepted 10 May 2015

Available online 6 June 2015

Keywords:

Ethyl chloride

Microreactor

Kinetics

Alumina

Chloroethane

Hydrochlorination

ABSTRACT

Ethyl chloride was synthesized by ethanol hydrochlorination in the temperature range of 240–340 °C. The reaction was performed in two serially coupled microreactors. Besides the main product ethyl chloride, several side-products were formed: ethylene, diethyl ether and acetaldehyde. A maximum ethyl chloride selectivity of 88.5% and 85.3% ethanol conversion were obtained at 300 °C (space time 0.154 s). Higher selectivities and conversions can be obtained at higher space times. Thermodynamic calculations were performed to assess the reversibility of the reactions and the equilibrium composition of the reaction mixture. The developed kinetic model accurately described the concentration profiles of all products in the studied range of temperature and initial reactant concentrations. All reactions were treated as reversible. Adsorption of ethanol and HCl was taken into account in the kinetic modeling. A catalytic effect of HCl concentration on the rates of the dehydration reactions was demonstrated.

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1. Introduction

Ethyl chloride or chloroethane is a chemical intermediate that is used as a general ethylation agent and local anesthetic. In the past, ethyl chloride was produced in large amounts to obtain the fuel additive tetraethyl lead (TEL) (Miller, 2000; Weissermel and Arpe, 2003). However, the demand has changed. Nowadays TEL is banned throughout the world and ethyl chloride production is sharply decreasing (Miller, 2000; Weissermel and Arpe, 2003). In the future, the main use of ethyl chloride will be cellulose ethylation. Ethyl cellulose is a versatile chemical that can be used amongst others as thickener, emulsifier, filmogen and flocculent (Majewicz and Podlas, 2000). In the past the main production

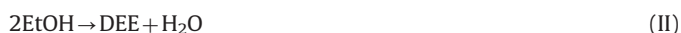
route of ethyl chloride was ethanol hydrochlorination, but due to high prices of ethanol, the main production route today is ethylene hydrochlorination. Further advantages of ethylene hydrochlorination are high selectivity and a possibility to be combined with other chlorocarbon plants by utilizing available HCl. However, with a shift to renewable resources, ethanol can become an attractive raw material again and its hydrochlorination could be a sustainable route for ethyl chloride production. For example, the on-site integration of ethyl chloride synthesis into a biorefinery is a very attractive option. Ethanol can be produced on-site in a biorefinery and further converted to ethyl chloride for the production of ethyl cellulose. Analogously, methyl chloride can be synthesized from methanol and used for the production of methyl cellulose. Ethyl and methyl celluloses can be valuable end-products of an integrated biorefinery.

In the hydrochlorination of ethanol several reactions can take place. The main reaction is the formation of ethyl chloride from ethanol and HCl (1). Ethanol dehydration reactions leading to the

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formation of diethyl ether (II) and ethylene (III) can occur (Knözinger and Köhne, 1964, 1966). Ethanol can be dehydrogenated to acetaldehyde (V) in small amounts. Furthermore, diethyl ether (VI) and ethylene (VII) react with HCl to form ethyl chloride. A range of other by-products such as ethane, butylenes, methane, propylenes (Kagymanova et al., 2011) can be obtained. In the current study they were detected in insignificant amounts. A chemically reasonable reaction scheme is displayed below.



From the viewpoint of thermodynamics, the system can be described with four independent reactions, (I)–(III) and (V). The remaining reactions are linear combinations of these reactions.

So far only one kinetic study on ethanol hydrochlorination has been published (Bukhanko et al., 2013). Neat and ZnCl₂ modified aluminas have been tested and activation energies for the hydrochlorination reaction of ethanol have been reported. However, the study focused on the catalyst development and screening of the reaction conditions. The kinetic model does not account for the formation of by-products as ethylene and diethyl ether. Thus, in this work the kinetics of ethanol hydrochlorination is thoroughly studied using a microreactor system.

Microreactors or microstructured reactors have at least one inner dimension in the submillimeter range (Ehrfeld et al., 2000). This leads to several advantageous features (Ehrfeld et al., 2000; Jähnisch et al., 2004). A very high surface-to-volume ratio results in an excellent heat transfer capability. The diffusion paths are typically short so that mass transfer is facilitated and local mixing is very rapid (Hessel et al., 2005). Due to the small inner volume the space time can be very short. Therefore, microreactors are ideal tools for a detailed kinetic study of fast reactions with a low amount of chemicals needed. Furthermore, the small inner volume of microreactors makes them inherently safe as explosions are inhibited. In case of chemical loss from the reactor only small quantities are released (Kolb and Hessel, 2004). For potential on-site production of ethyl chloride microreactors are an interesting option to provide high safety and high space efficiency due to the suppression of diffusion limitations.

The use of microreactors for the kinetic study of ethanol hydrochlorination has several advantages. In a recent study on the kinetics of methanol hydrochlorination, the internal diffusion

limitations inside the catalyst layer were investigated by very detailed simulations (Schmidt et al., 2013). It was shown that the reaction is limited by internal diffusion. While in a microreactor with a coating thickness of 15 μm intrinsic kinetics can be assumed, at a catalyst layer thickness of 50 μm the effectiveness factor dropped to 0.69. At a layer thickness of 2 mm, which is typical for catalyst pellets, the effectiveness factor is merely 0.03. Because the rates of ethanol and methanol hydrochlorination are comparable, the use of microreactors or fine catalyst powder is necessary to reveal the intrinsic kinetics. However, compared to a tubular reactor packed with fine powder, the microreactors offers a superior temperature and space time control. Furthermore, the amounts of chemicals used to achieve short space times is substantially reduced.

While ethanol hydrochlorination is barely investigated, ethanol dehydration reactions on alumina are intensively studied and results can be used to clarify the reaction mechanisms in ethanol hydrochlorination. Knözinger and Köhne reported in early studies that the formation of diethyl ether is preferred at lower temperatures while ethylene formation is favored at higher temperatures (Knözinger and Köhne, 1964, 1966). The kinetics of ethylene and diethyl ether formation has been discussed by Morávek and Kraus (1984) and Golay et al. (1998). However, the role of water and ethanol adsorption on the reaction rates of ether and ethylene production is still under discussion. Water is thought to compete with ethanol on the adsorption sites on alumina (Christiansen et al., 2013; DeWilde et al., 2013; Morávek and Kraus, 1986). According to DeWilde et al. (2013) the activation energies of both reactions are similar and the selectivity to diethyl ether or ethylene depends on the surface coverage of ethanol on alumina. In the study of Kagymanova et al. (2011), ethanol adsorption is not taken into account. However, the adsorption of the reactants is important for the description of reactions of ethanol/HCl on the alumina surface. Surface ethoxy groups are assumed to be the active species (Golay et al., 1998; Phung et al., 2014). Acetaldehyde is not formed in significant amounts on alumina (Knözinger and Köhne, 1966; Erdöhelyi et al., 2006). The goal of the present work is to determine the kinetics of ethanol hydrochlorination and side reactions in a microreactor system.

2. Experimental section

2.1. Experimental setup

The reactor setup consisted of two stainless steel gas-phase microreactors (GPMR-mix, purchased from Institut für Mikrotechnik Mainz, supplier: Microinnova) coupled in series. The microreactor and the microchannel platelets are shown in Fig. 1. The reactor has two zones, a mixing and a catalytic zone, each equipped with ten stainless steel microstructured platelets. The

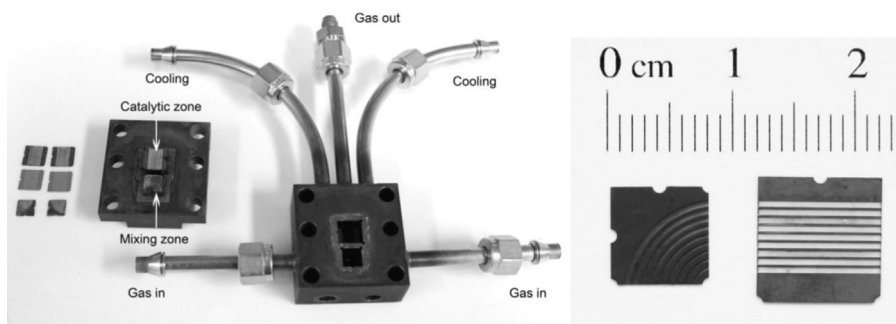


Fig. 1. Left: Microreactor with mixing and catalytic chambers. For the second microreactor, one of the gas inlets was closed by a stainless steel cylinder. Right: Close-up on microchannel platelets, mixing platelet and catalyst coated platelet.

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