458d Adsorptive Ozonation of Organic Pollutants in Zeolite Monolith: a Kinetic Study

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Abstract

The enhancement of oxidation rate of persistent organic pollutant by adsorptive ozonation process with a zeolite monolith was demonstrated in this study. The dissolved ozone was concentrated in the micropores of the zeolite monolith as well as persistent organic pollutants such as acetaldehyde, and their reaction rates were increased significantly. Furthermore, the organic pollutants could be mineralized in this process, which was difficult in the bulk phase ozonation. On the basis of the experimental outcomes, a numerical model was developed for predicting the decomposition of organic pollutants in the zeolite monolith packed column. Using this model, the optimum operation condition was discussed.

1. Introduction

Ozonation of organic pollutants in aqueous media have been extensively investigated by many researchers [1,2,3]. However, the low solubility of ozone in water was found to be a major difficulty in the ozonation processes. Advanced oxidation processes (AOPs) have been suggested [4-6] to enhance the decomposition rate of persistent organic pollutants. In AOPs, OH radical was generated from O_3 by adding H_2O_2 or radiating UV light etc., and as a result, the decomposition rate in AOPs was increased significantly, because of the high oxidation potential of OH radical. However, OH radical also could react with non-targeted substrates, and as a result, undesirable by-products were produced in some cases.

In our previous study, a novel ozonation process using zeolite adsorbents, adsorptive ozonation, was proposed to resolve those problems [7]. The organic pollutants and ozone could be adsorbed in the micropores. As a result, those concentrations become extremely higher than in bulk phase. Therefore, the apparent reaction rate of them could be increased. The feasibility of adsorptive ozonation for trichloroethene decomposition was verified in our previous study [7]. However, the behavior of decomposition products was not clear. In addition, the contact method of ozone or organic pollutants with the zeolite was demanded to improve. To resolve this, the zeolite monolith was proposed instead of the zeolite. The objective of this study is to clarify the decomposition kinetics of persistent organic pollutants in a zeolite monolith, and to estimate the deterioration factors in the process. Acetaldehyde was used as a model persistent organic pollutant in this study.

2. Materials and methods

2.1 Materials

The adsorbents employed in this study were powdery high silica zeolites, HiSiv 3000 (SiO2/Al2O3 > 1000, UNION SHOWA K. K., Japan), and a zeolite monolith. The zeolite monolith was prepared by coating the HiSiv 3000 powder on a cordierite honeycomb monolith support (IWAO JIKI KOGYO Co., Ltd., Japan)(10 mm x

The physical properties of the polymer product determine to a large extent its processability and applications. A large number of properties are directly related to the molecular mass distribution (MMD) of the polymer product. Besides the MMD, the polymer microstructure also plays an important role and influences to a large extent the thermal stability of the polymer product. Most of the thermal degradation

reactions start at thermally labile structural segments of the polymer chains, i.e. internal allylic and tertiary chloride structural defects, formed during polymerization (cfr. Figure 1).

In the past 30 years, several mathematical kinetic models have been developed to describe the heterogeneous free-radical suspension polymerization of vinyl chloride (Xie et al., 1991, Kiparissides et al., 1997). However, little effort has been made to model the formation of structural defects during the polymerization process. As the PVC-polymer microstructure affects its physical properties, an understanding of the interplay between process conditions and the number and type of structural defects formed during the polymerization process is important to control the quality of the PVC-polymer product.

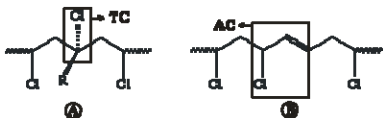

Figure 1 Structural defects in poly(vinyl chloride): A) Tertiary chloride (TC), B) Internal allylic chloride (AC). (R= short or long chain branch)

In the present contribution a fundamental microkinetic model describing the suspension polymerization of vinyl chloride taking into account diffussional limitations is presented. The model allows to predict the conversion, the MMD and the structural defects content as a function of batch time over a wide range of industrially relevant conditions. To achieve this, the free radical polymerization of vinyl chloride was modeled at the elementary reaction level. All elementary reactions occurring during the VCM free radical polymerization were grouped into five reaction families consisting of forward and backward steps, cfr Figure 2.

-Bond dissociation. The bond dissociation reaction involves the breaking of a bond to form two radical structures. For this reaction to occur, the breaking bond needs to have a sufficiently low bond dissociation energy.

-Radical recombination. The radical recombination reaction family includes termination reactions in which two radicals combine to form one molecule. The recombining radicals can be carbon, chlorine and oxygen radicals.

-Beta-scission reaction. The beta-scission reaction family involves the cleavage of a bond in beta-position to the radical and results in the formation of a double bond and a new radical. The beta-scission reaction is mainly responsible for the formation of internal double bonds and its occurrence thus largely determines the allylic content of the polymer product.

-Radical addition to a carbon-carbon double bond. The addition of a radical to a double bond comprises the addition of a carbon, chlorine or oxygen radical to a carbon-carbon double bond. In case of the addition of a carbon centered radical to vinyl chloride monomer, a distinction can be made between an addition to the double bond at the non-substituted carbon atom (head-to-tail, HT) or at the substituted carbon atom (head-to-head, HH).

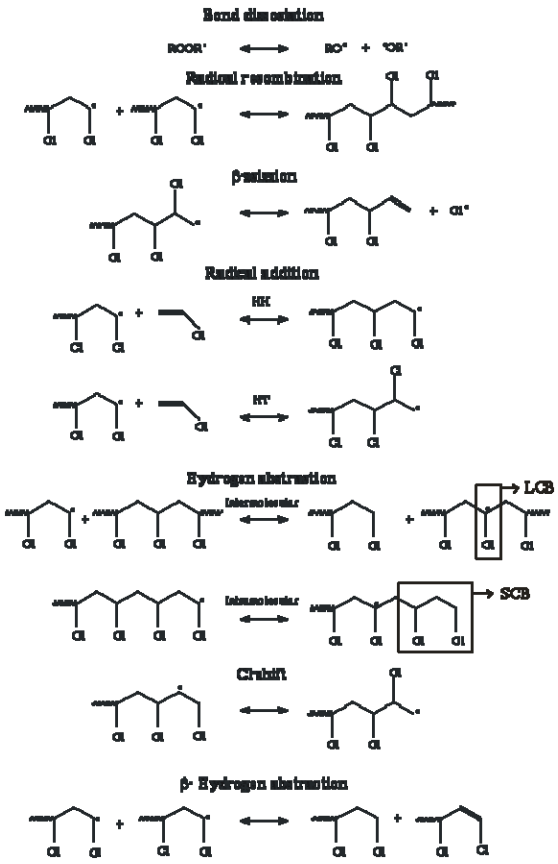

Figure 2 Overview of the elementary reaction types incorporated in the kinetic model describing the suspension polymerization of vinyl chloride.

-Hydrogen abstraction. This reaction family involves the radical abstraction of hydrogen from molecular species. A distinction between inter- and intramolecular hydrogen abstraction can be made. The intermolecular hydrogen abstraction leads to long chain branching (LCB), while the intramolecular hydrogen abstraction forms short chain branches (SCB) (cfr. Figure 2).

-Cl-shift. This reaction family involves the transfer of a chlorine atom in beta-position to the radical center.

-Beta-hydrogen abstraction. This reaction family, also known as disproportionation, involves the termination of two end-chain radicals to form two non-radical polymer species.

By applying this set of elementary reactions to all species in the reaction mixture the polymerization reaction network can be generated. Since polydisperse, high molecular weight materials are formed, polymeric and radical chains of thousands of different chain lengths with different chemical compositions are formed. Tracking each of these distinct species individually is computationally too demanding. To overcome this difficulty, a population-balance-based model has been developed (Kruse et al., 2002).

It was found that all radical structures formed during the polymerization process can be classified into a limited number of groups according to the structure of their radical center. The formation of different structural defects in the polymer product can be directly linked to the presence of these distinct radical types in the reaction mixture, as is illustrated in Figure 3.

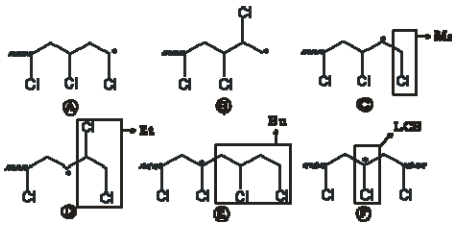

Figure 3 Overview of radical types considered in the kinetic model describing the suspension polymerization of vinyl chloride. (Me=chloromethyl, Et= 1,2-dichloroethyl, Bu= 2,4-dichloro-n-butyl, LCB=long chain branching)

To track the evolution of the monomer conversion, the molecular weight changes and the structural defects content, mass balances were derived for monomer, dead and live polymer species. The method of moments was applied to model molecular weight changes. The mass balances, as well as the expressions to calculate the structural defects concentration, contain the total concentration of the different radical types and the apparent rate coefficients of all elementary reactions.

The total concentration of each radical type was determined based on the total mass balance of each radical type, by summing over all chain lengths.

Each apparent rate coefficient is built up from two contributions: the intrinsic rate coefficient and a diffusion contribution. The latter is determined using the Smoluchowski expression in which the diffusion coefficients are calculated using the free volume theory (De Roo et al., 2004).

The Arrhenius parameters of the intrinsic rate coefficients can be obtained by regression of experimental data for monomer conversion, moments of the molecular mass distribution and structural defects content (De Roo et al., 2005). The latter information can be obtained from ^{13}C NMR analyses. This technique allows the measurement of defect concentrations.

By representing the chemistry in terms of five reaction families a limited set of parameters to be estimated simultaneously was obtained. The kinetics within each family were captured in terms of a pre-exponential factor and the parameters of a linear free energy relationship, which relates the activation energy to the value of an appropriate reactivity index. By applying such a linear free energy relationship, the structure of the reactants and products is linked to the elementary step reaction rate coefficients.

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