Adhesion and agglomeration of catalyst particles in three phase reactors
van der Zon, M.

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Introduction

In the chemical industry gas-liquid-solid reactors are abundantly used, for instance in hydrogenation and oxidation reactions. In the three phase reactors the solid phase is often the catalyst. Industrial practice learns that for carbon supported catalysts the reaction rates in three phase reactors may differ for different batches of activated carbon. This might be caused by a difference in physical properties, like hydrophobicity, for different batches produced activated carbon particles. In this thesis the impact of the hydrophobicity of the activated carbon particles and the reaction media on the performance of a three phase reactor is described.

As a result of the hydrophobicity of the activated carbon, catalyst particles based on carbon supports may segregate from an aqueous phase in a three phase reactor. This segregation then either results in particle agglomeration or in particle to bubble adhesion (Figure 1.1). The segregation of the hydrophobic catalyst particles in aqueous media affects both the conversion rate and the operation of the reactor. In case of adhering catalyst particles, these particles tend to be present in the liquid film around the bubble. This may result in an increased mass transfer rate of the gaseous reactant as suggested by Vinke et al. (1993). For a mass transfer limited reaction this will lead to an increased conversion rate. Agglomeration on the other hand results in an increased effective particle diameter, leading potentially to a decreasing conversion rate when the reaction is mass transfer limited.
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Figure 1.1. Schematic representation of the behaviour of hydrophobic catalyst particles in a three phase slurry reactor.

To predict the overall impact of particle segregation, it is important to investigate both agglomeration and particle to bubble adhesion. Chapter 2 describes the impact of adhesion and agglomeration on mass transfer under ambient conditions. Variations in the hydrophobicity of an activated carbon particle may lead to a different net effect of adhesion and agglomeration and may therefore provide an explanation for variations in conversion rates, which are observed for different batches of carbon supported catalysts. The impact of the hydrophobicity of activated carbon particles on the mass transfer enhancement is described in Chapter 7.

Adhesion can be investigated under stagnant and under non-stagnant conditions. Vinke et al. (1991) and Wimmers et al. (1988) introduced Bubble Pick Up (BPU) equipment. In this method a bubble at a GC needle is dipped into a slurry of catalyst particles and slowly withdrawn. The bubble with any adhering particles is projected. From this projection the bubble coverage angle can be measured. Under non-stagnant conditions a flotation column can be used to determine the bubble coverage (Drzymala et al. (1994)). In Chapter 3 a comparison between stagnant and non-stagnant adhesion measurements is made. A model to describe this particle to bubble adhesion is introduced in Chapter 6.
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Agglomeration is investigated under stagnant conditions using a light microscope as described in Chapter 2. Besides these experiments, also mass transfer experiments described in Chapter 2 are used to show the possible impact of agglomeration on the performance of a three phase reactor.

Both types of segregation behaviour, agglomeration and adhesion, of particles in aqueous solutions are affected by the hydrophobicity of the surface. The most commonly used parameter to describe the hydrophobicity of substances is the three phase contact angle between liquid, solid and gas. For the determination of this parameter a flat surface is needed. The activated carbon particles used as catalyst particles are usually very porous and very small in size. Washburn introduced a method for determination of the three phase contact angle of small particles (Heertjes et al. (1967)). The sedimentation method introduced by Vargha-Butler et al. (1985) can also be used to determine the three phase contact angle. Besides this three phase contact angle there are also some other methods to investigate the hydrophobicity. One of them is the Weitkamp method (Weitkamp (1993)). This method is based on the competitive adsorption of toluene and water vapour. As mentioned before, the amount of oxygen containing groups determines the hydrophobicity of activated carbon particles. Therefore, it is also possible to investigate the hydrophobicity by FTIR. To this end the FTIR peak representing carboxylic groups is compared to the peak representing bulk aromatic groups. Heinen et al. (2000) demonstrated that the FTIR method and the Washburn method produce similar trends. These methods are described and compared in Chapter 4.

Besides the effect of adhering particles on the external mass transfer, particle to bubble adhesion also affects the hydrodynamics in a three phase reactor as investigated in Chapter 5. The presence of particles in a three phase reactor is known to result in a decrease of the gas holdup, arising from the increased apparent viscosity and density of the slurry phase (Krishna et al. (1997)). However, the presence of such particles at the bubble surface also affects the bubble coalescence rate. Banisi et al. (1995) show that in the presence of hydrophobic particles the gas holdup is higher compared to the gas holdup in the presence of non-adhering particles, like silica. This indicates that the presence of hydrophobic particles also tends to affect the overall hydrodynamics.
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References


