

PHASE TRANSFER CATALYZED REACTION FOR A NOVEL ORGANOSILANE COUPLING AGENT

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Abstract

A process was recently developed involving a phase transfer catalyzed (PTC) reaction to synthesize a novel organosilane coupling agent. PTC offers many advantages for organosilane synthesis such as lower cost, improved safety, and reduced environmental footprint. A lab reactor was designed to conduct process development studies with the same L/D and agitator and baffle geometry as the plant reactor. Mixing was simulated based on power per unit volume. With this geometrically similar reactor and simulation of mixing behavior we were successful in predicting reaction kinetics, crystallization behavior, and product impurity profile for scale up. Understanding the rate limiting factors for this solid liquid PTC system was critical to optimizing reaction conditions, including mixing rate, catalyst structure, and solvent selection. The presence of polar protic species in this reaction is a critical factor affecting reaction kinetics, crystallization behavior, and filtration performance.

Keywords

Phase transfer catalysis, reaction kinetics, mixing, mass transfer, solvent, reaction mechanism, crystallization, process development, solvent, polar protic

Introduction

A novel acryloxysilane has been scaled up via reaction of metal carboxylate with haloorganoalkoxysilane using quaternary ammonium based phase transfer catalyst (PTC). This reaction would be very inefficient without a phase transfer catalyst and require expensive and toxic polar aprotic solvents such as DMSO, DMF, and NMP. (Sasson and Neuman, 1997) However, with PTC technology the reaction proceeds rapidly to high conversion using a wide range of organic solvents, reducing cost and environmental footprint, and improving safety. Optimization of mass transfer is of particular interest with this heterogeneous solid/liquid reaction. After synthesis of crude acryloxysilane, metal halide salt formed during the reaction is removed by filtration. Understanding of the factors affecting crystallization behavior is therefore important due to the impact on filtration performance. The presence of trace levels of polar protic species had a significant impact on reaction behavior and crystallization of the metal halide by-product.

Mass Transfer Effects

The overall rate of reaction in solid/liquid PTC systems is often dependent on mixing intensity, especially below a certain critical agitation rate. (Naik, 1998) To understand the dependence of reaction rate, yield, and selectivity on mixing intensity several batches were made using varying agitation rates. As seen in other PTC reactions the reaction rate increases with higher mixing until reaching a critical agitation rate, above which the reaction rate remains constant with further increases in mixing intensity. (Cognis, 2009) For this process development study it was critical to run the reaction above this critical mixing rate to simulate behavior in the production scale reactor. Below this point significant differences in kinetics, product distribution, and by-product formation could occur resulting in data irrelevant to the actual production process.

Initial studies using a reactor with different geometry and mixing intensity than the plant reactor resulted in

significant differences in reaction profiles, crystallization, and filtration behavior. To enable process development under conditions that would scale effectively to the plant a lab reactor was designed with the same L/D, agitator type and geometry, and baffling as the reactor in production. Use of this geometrically similar lab reactor was successful in predicting reaction kinetics and crystallization behavior at the production scale. Mixing was found to scale effectively based on power per unit volume. This lab reactor also provided more accurate prediction of product characteristics such as particle size of the salt by-product and product impurity profile. Higher oligomeric by-product formation was observed in the lab reactor, which accurately predicted the production scale process. This observation is consistent with literature reports linking high mixing rate with increased hydrolysis in other PTC reactions. (Cognis, 2009)

Rate Limiting Behavior

When optimizing PTC reaction conditions a top priority is to determine whether a reaction is limited by anion transfer (T Reaction) or by the rate of the intrinsic reaction (I Reaction). (Starks et. al., 1994) This information facilitates identification of optimal catalyst structure, solvent, and other conditions for the reaction. In the acryloxy synthesis several indications of I reaction behavior were observed. The above mentioned independence of reaction rate of mixing intensity (above a relatively low critical mixing rate) is one example. Improved yield and selectivity observed with more organophillic quaternary ammonium catalyst as well as the pKa range of the conjugate acid of the carboxylate anion provide further evidence that the reaction is intrinsic rate limited. Another indication is that catalysts with more accessible cations on nitrogen do not improve reactivity or yield as would be expected with a transfer rate limited reaction. (Starks et. al., 1994)

Effect of Moisture

Lot to lot variation in metal carboxylate resulted in significant challenges during scale up. Moisture content in this critical raw material is an important factor directly affecting the reaction kinetics and indirectly affecting downstream filtration performance. As shown in figure 1, the reaction rate is highly dependent on moisture content with the rate constant increasing nearly three-fold when water content is decreased by 3000 PPM. The change in moisture and subsequent reaction rate also impacts the particle size of salt precipitating during the reaction. A four-fold decrease in particle size of the salt by-product occurs with the 3000 PPM decrease in moisture. Understanding of this relationship was instrumental in reducing filtration time by more than 3 times.

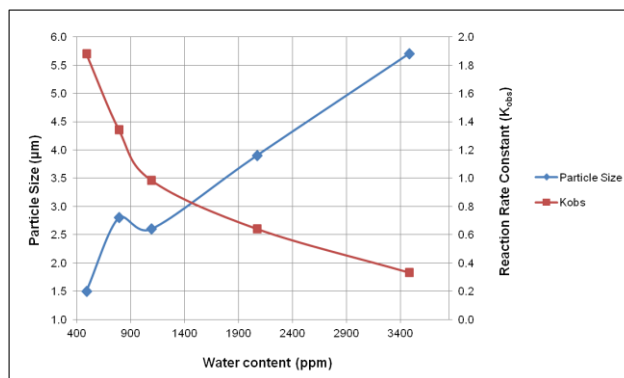


Figure 1. Effect of water content on reaction rate and particle size of salt formed during the reaction

Conclusions

Lab studies showed reactor geometry and mixing to be important factors for scale up. Using the same L/D and mixing (power per unit volume) in the lab as expected for the plant reaction was successful in achieving predictable scale up of the acryloxysilane process. Understanding of rate limiting behavior of this PTC reaction facilitated optimization of the process through appropriate catalyst and solvent selection and mixing conditions. Polar protic species strongly affect the reaction rate, crystallization, and downstream filtration performance. By optimizing moisture content and other polar protic species significant reduction in batch time and economic improvement was achieved.

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