LIQUID-LIQUID-SOLID SLUG FLOW IN CAPILLARY MICROREACTOR

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Summary

The hydrodynamic and particle behaviour in slug flow was analysed using fluorescent particles and particles of typical catalyst supports in various biphasic liquid-liquid systems. Typically, no complete circulation of particles over the full slug length was observed. The principle of suspension catalysis in a capillary reactor slug flow was demonstrated experimentally for a heterogeneous catalytic transfer hydrogenation of m-nitrotoluene with aqueous potassium formate.

Keywords

Multiphase and particulate reactors, Process intensification, Micro-reactors

Introduction

Heterogeneous catalysis with suspended catalyst particles is a topic seldom addressed in mainstream microreaction engineering, with its emphasis on fluid reaction systems. The use of heterogeneously catalysed reactions has so far mainly been restricted to immobilised solid catalysts, either in micro-fixed-bed or catalytically coated wall reactors, mostly with single phase flow of gas or liquid. Suspended particles in microreactors have only been examined for the preparation of pigments, which are formed as non-reactive nanoparticles with densities close to that of the surrounding liquid, and thus of limited significance in applications for reactions with suspended catalyst particles.

The introduction of fine heterogeneous catalyst particles into two phase slug flow in capillary reactors offers clear benefits for both catalyst utilisation and recovery. Taylor-flow circulation within the slugs ensures excellent catalyst accessibility. Particles can be retained within one of the two liquid phases by virtue of their wetting properties, which may be modified accordingly if necessary. Since catalyst separation is by wettability, rather than filtration or sedimentation, very small catalyst particle sizes of only a few microns with high specific surface areas and quasi-homogeneous properties can be used.

An understanding of the hydrodynamic and particle behaviour in slug flow is essential for evaluating such an implementation of suspended catalysts. In addition to experimental and simulation studies using various particles, the principle described was demonstrated experimentally in a capillary reactor for a heterogeneous catalytic transfer hydrogenation reaction system.

Slug Flow Particle Hydrodynamics

Particle motion and mixing in slug flow is mainly caused by internal circulation induced by shear forces at the capillary wall. Thus, internal circulation and particle movement was analysed using fluorescent particles in various biphasic liquid-liquid systems. Further the flow patterns for particles of typical catalyst supports in a toluene-water-system were studied.

Internal circulation in slug flow

Hydrophilic, fluorescent polystyrene particles with a diameter of 10 µm were suspended in aqueous solutions and observed in slug flows with organic liquids or air as the second fluid, for various viscosities and surface tensions between the two liquids. In a PTFE capillary with internal diameter of 1.0 mm, the organic liquid forms a continuous, wall-wetting phase and the aqueous phase is present as discrete slugs. In a PTFE capillary with internal diameter of 1.0 mm, the organic liquid forms a continuous, wall-wetting phase and the aqueous phase is present as discrete slugs. Typically, no complete circulation of particles over the full slug length was observed and a circulating zone was usually formed at the leading end of the slug, while the rear portion is

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stagnant. The extent of the active vortices is very sensitive to liquid properties and thus to changes in the wall film. By adding small amounts of ethanol or saccharose to the water, the circulating zone can be drastically expanded or eliminated, respectively (Fig. 1). When the aqueous solution constitutes the continuous and wall-wetting phase, as with glass capillaries, using organic liquids or air as the dispersed phase, complete circulation is achieved.

**Particle behaviour in toluene-water-slug flow**

Silicon dioxide or aluminum oxide particles suspended in the aqueous phase follow the internal circulation streamlines almost exactly. A higher concentration is observed at the bottom due to gravitational forces. Similarly to the findings with the fluorescent particles, a stagnant zone at the end of the slug was identified. At low loadings, a second vortex arises in this zone with reverse rotation to the circulation in the forward section, which becomes stagnant at higher loadings (Fig. 2). An exchange of particles takes place between the two zones. At the flow rates investigated (1 - 8 ml/min) the distribution of the particles between the zones only depends on particle loading.

Particles of carbon or activated carbon (ca. 20 - 50 µm) with and without palladium catalyst suspended in toluene formed a cap around the rear end of the aqueous slug in a PTFE capillary with an internal diameter of 1.6 mm. At low loadings (< 2 g/L) a ring of particles first arises, which then extends along the organic wall film in the direction of flow to yield an almost enclosed sheath at higher loadings (> 10 g/L) (Fig. 3). Residual suspended particles or agglomerations at the other end of organic slug completely merge with this cap during the flow. Particles in this 'swarm' are in a state of continuous motion relative to one another, whilst the entire cap itself rotates axially.

**Suspension Catalysis in Liquid-Liquid Capillary Reactor**

The heterogeneously catalysed transfer hydrogenation of m-nitrotoluene to m-toluidine with potassium formate as a hydrogen donor was carried out at 70 °C as a test reaction in a capillary reactor with an internal diameter of 1.6 mm. This three phase system is comprised of the aqueous formate solution, nitrotoluene in toluene as the organic phase and 10% palladium on carbon particles suspended in the organic phase. Reagent concentrations were adjusted according to their affinity for the catalyst active sites, while flow rates (1.5 - 3.0 ml/min) and catalyst loadings (4 – 8 g/l) were varied. The hydrodynamic behaviour of the system corresponding to that described above for carbon particles in toluene-water (Fig. 3). Nitrotoluene conversions of 43 % were achieved within 23 min, comparable to those in a conventional intensively stirred reactor at somewhat longer reaction times (47 % in 20 min).

**References**

