**Reaction and kinetic studies of homogeneously catalyzed benzyl alcohol oxidation in a gas-liquid slug flow microreactor**

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**Highlights**

* Aerobic oxidation of benzyl alcohol was studied over a homogeneous Co/Mn/Br catalyst.
* Wetted and dewetted gas-liquid slug flows were identified in the microreactor.
* A kinetic expression of benzyl alcohol oxidation to benzaldehyde was established.
* A reactor model was developed under mass transfer limited conditions.

**1. Introduction**

Slug flow processing in microreactors brings significant transport intensification (e.g., enhanced heat and mass transfer rates) and precise process control (e.g., regular flow pattern, narrowed residence time and uniform reaction temperature) that benefit chemical synthesis in multiphase systems. Thus, it represents an attractive means for the intensification of a variety of gas-liquid reactions (including typically selective oxidation and hydrogenation reactions), as well as kinetic investigations thereof [1-3]. In this work, a model reaction, the aerobic oxidation of benzyl alcohol to benzaldehyde in the presence of a homogeneous Co/Mn/Br catalyst, has been studied in a microreactor in the gas-liquid slug flow regime. The microreactor performance has been experimentally characterized under various slug flow conditions, which was interpreted based on the developed kinetic expression and reactor model.

**2. Methods**

The reaction was performed in a capillary microreactor made of polytetrafluoroethylene, using benzyl alcohol (dissolved in acetic acid) as the substrate, oxygen or air as the oxidant, a mixture of Co(OAc)2, Mn(OAc)2 and NaBr as the homogeneous catalyst. The reaction temperature was up to 150 oC and pressure up to 5 bar. The pictures of slug flow were recorded with a digital camera. The collected liquid samples from the microreactor outlet were analyzed by gas chromatography.

**3. Results and discussion**

Under the investigated conditions, the reaction was found highly selective towards benzaldehyde. Two different types of gas-liquid slug flow were identified: wetted flow (characterized by a complete liquid film surrounding the bubble) and dewetted flow (characterized by a partially wetting liquid film surrounding the bubble); the latter flow suffered from a limited interfacial area available for mass transfer. The transition from wetted to dewetted slug flow depended on the flow velocity and gas-liquid flow ratio (i.e. the bubble length). By a fine tuning of the reaction temperature and mass transfer (i.e., via the presence of wetted or dewetted flow), the reaction behaviour fell in either kinetic or mass transfer limited conditions. The experimental results at lower reaction temperatures were used to develop a simplified kinetic expression. The experimental results at higher reaction temperatures were well described by the developed microreactor model. The model considers a fast reaction regime, where mass transfer details (under wetted and dewetted slug flows) are based on the literature correlations and the reaction kinetics is based on the current work.

**4. Conclusions**

Aerobic oxidation of benzyl alcohol to benzaldehyde was studied over a homogeneous Co/Mn/Br catalyst in the microreactor operated under wetted and dewetted gas-liquid slug flows. The reaction was found under either kinetic or mass transfer limited conditions, depending on the reaction temperature. The experimental results at lower temperatures allowed to establish a simplified kinetic expression. This expression, with a further consideration of mass transfer details in slug flow, enabled the formulation of a microreactor model describing the experimental results at higher temperatures.

**References**

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