

Continuous SiC heat-exchanger reactor as a relevant tool for the investigation of catalytic epoxidation kinetics

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Highlights

- Ti/SiC and Ti/SiO₂ trilobe catalysts with high activity, selectivity, and stability in cyclohexene epoxidation
- Kinetic modelling of cyclohexene epoxidation
- Continuous SiC heat-exchanger reactor for reaction kinetic studies

1. Introduction

Fine control of the operating temperature is still an issue for highly exothermic catalytic reactions, which can result in hot spots – reducing process selectivity and accelerating the catalyst deactivation, up to thermal runaway, leading in turn to loss of confinement of toxic and/or flammable substances. Most processes in the specialty chemical industry are batch or semi-batch operations. These types of reactors can offer large production volumes and are quite flexible. However, controlling the temperature and heat transfer becomes more difficult as the size of the reactor increases. A compact, intensified, continuous heat-exchanger reactor could avoid the risk of thermal runaway making the process much safer [1]. In this study, we investigate the performance of a heat-exchanger (HEX) reactor made of silicon carbide (SiC) enclosing a milli-fixed bed. Due to its characteristics, which combine an extraordinary chemical resistance even against highly corrosive media together with very high thermal conductivity [2], silicon carbide is expected to be a highly innovative option. Moreover, processes involving heterogeneous catalysis are preferred in the industry, because they allow better atom economy, simple separation of products, and easier recycling of the catalyst. To optimize heat transfer and avoid hot spots, the same material (SiC) will be used for both the reactor and the catalyst support. This integration is made possible by the commercial availability of SiC catalyst carriers of various shapes and a suitable grafting strategy for the active phase.

2. Methods

The epoxidation of cyclohexene using an organic peroxide was selected as a representative exothermic reaction. This process holds industrial significance, often achieving complete conversion of the alkene, yet remains attractive for its environmentally friendly operation and increased selectivity. The reaction involves the epoxidation of cyclohexene (CH) with cumene-hydroperoxide (CHP), resulting in cyclohexene epoxide (E) and cumyl alcohol as a by-product. Cyclopentyl methyl ether (CPME) was used as a solvent. Various catalysts (in the form of millimeter-sized pellets) were tested in a 400 mL glass batch reactor operating under controlled temperature, equipped with a condenser and a catalyst basket. Gas chromatography was employed to quantify reaction products and monitor progress. Mild operating conditions were chosen to align with industrial needs: $70 \leq T \leq 90^\circ\text{C}$. The same reactor was utilized to assess catalyst stability. Reaction kinetics was explored to identify optimal conditions for conducting the epoxidation reaction in a continuous mode, using a catalytic heat-exchanger reactor intended to enhance safety and reduce energy and material consumption. This compact and multifunctional reactor features a central section with a reactive plate containing a milli-fixed bed ($d_R = 8$ mm), flanked by two cooling plates housing the utility fluid. An experimental campaign was conducted, varying temperature, reactant concentration as well as liquid flow rate, and the epoxide yield was compared to that measured in the batch stirred reactor at the same catalyst contact time.

3. Results and discussion

Ti/SiO₂ and Ti/SiC supported catalysts (20 and 200 m²/g respectively, 0.7-2 wt.% Ti) developed by ICGM demonstrated high activity, nearly complete selectivity in epoxide production, and stability over successive epoxidations (cf. Fig. 1). Extensive experimental data were utilized to determine the kinetics

of the reaction. It could be fitted by a rate expression of Langmuir-Hinshelwood type, with $r = \frac{k K_{\text{CHP}}[\text{CHP}][\text{CH}]}{1 + K_{\text{CH}}[\text{CH}] + K_{\text{E}}[\text{E}] + K_{\text{CHP}}[\text{CHP}]}$ [3], [4], showing an inhibition by the reaction product. This rate law served as basis for the batch to continuous transposition, allowing the HEX reactor to operate under isothermal conditions with quantitative substrate conversions. To achieve this, the following conditions were explored: $70 \leq T \leq 90^\circ\text{C}$, with a reference liquid flow rate \dot{m}_{liq} of 1 kg/h. The measured outlet epoxide yield conformed to the predictions of a plug-flow reactor model (as expected from preliminary tracing measurements) without external mass transfer limitations. Furthermore, as depicted in Fig. 2, the species concentration profiles over catalyst contact time (WHSV^{-1}) closely matched those predicted by the ideal model.

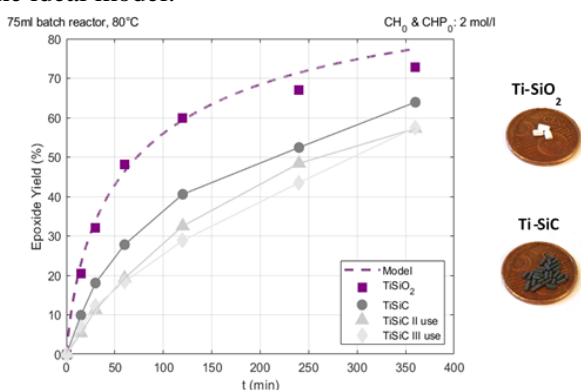


Figure 1: comparison of epoxide yield vs. time for Ti/SiO₂ and Ti/SiC trilobes in batch stirred reactor ($T = 80^\circ\text{C}$, $V_{\text{liq}} = 75 \text{ mL}$, $V_{\text{cat}} \sim 3.5 \text{ mL}$, CPME solvent)

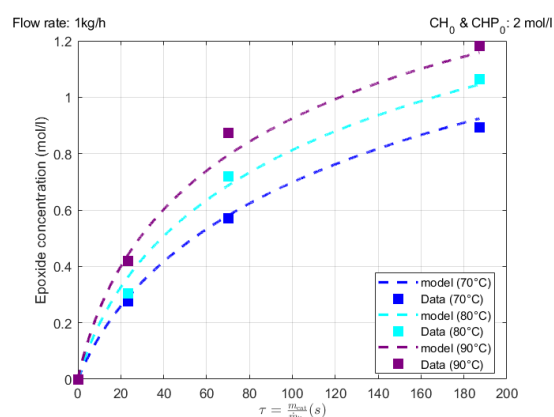


Figure 2: measured and predicted epoxide concentration profiles along the continuous reactor, for different temperatures ($\dot{m}_{\text{liq}} = 1 \text{ kg/h}$, $m_{\text{cat,tot}} = 52.8 \text{ g}$, Ti/SiO₂, CPME solvent)

4. Conclusions

Ti/SiO₂ and Ti/SiC catalyst pellets demonstrated activity in the epoxidation of cyclohexene at temperatures below 100°C. Expressions for the apparent rate law were developed, allowing the prediction of epoxidation yields over a wide range of conditions. Successful transposition from batch to continuous process was accomplished using the HEX reactor achieving isothermal conditions and ideal hydrodynamic behavior. The HEX reactor will be applied to study cyclooctene epoxidation on Ti/SiC at higher temperatures and without solvent. Dynamic tests with variations in solution composition will also be carried out to gain insight into the reaction mechanisms.

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Keywords

“Cyclohexene epoxidation”; “Silicon carbide”; “Heat-exchanger reactor”, “Process intensification”.

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