Comparison of a monolith and a confined Taylor flow (CTF) reactor for propene epoxidation

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ABSTRACT

Heterogeneous catalytic epoxidation of propene to propene oxide with hydrogen peroxide was investigated in a monolith and a confined Taylor flow (CTF) reactor in which titanium silicalite (TS-1) catalyst was coated on the walls. The influence of gas and liquid superficial velocity on the hydrodynamic characteristics of the monolith and CTF reactor was also investigated under Taylor flow regime at atmospheric and high pressure. The reactors showed distinctly different hydrodynamic properties which in turn led to different performance for propene epoxidation. The production rate of propene oxide was higher in the monolith reactor due to its larger catalyst coating area, larger mass-transfer surface area and more frequent recycling of liquid flow. A variation of reactor column structures confirmed that the propene oxide production was highly dependent on the catalyst coating area and cross-sectional area of the reactor column. High operating pressure made a significant impact on the length of Taylor bubbles and the propene oxide production rate was found to increase in proportion to the operating pressure.

1. Introduction

Propene is an important petrochemical feedstock with the second largest volume after ethene in the chemical industry and its demand has increased rapidly at an annual growth rate of 4–5%. Its global production capacity reached 109 million tonnes in 2014 and is anticipated to expand to 165 million tonnes a year by 2030 [1,2]. Propene is used to manufacture a variety of chemical products such as polypropene, acrylonitrile, propene oxide, cumene, acrylic acid, oxo-alcohols and isopropyl alcohols, among which propene oxide accounts for approximately 10% of propene consumption as the third largest derivative. Subsequently, propene oxide is employed for the production of polyether polyols (65%), propene glycols (30%) and propylene glycol ethers (4%) and the propene oxide market has also grown fast in conjunction with propene market expansion [3].

The chlorohydrin process that has the longest history in the propene oxide industry occupied the majority of propene oxide production in 1970. Since then, due to its environmental liabilities, the hydroperoxidation process snatched attention and achieved a similar production capacity share in 2000. However, the hydroperoxidation process suffers from the marketability of co-products that are produced simultaneously in quantity. As a result, considerable attention has been paid to the direct epoxidation of propene using hydrogen peroxide oxidant (HPPO: hydrogen peroxide propene oxide) as an eco-friendly

and profitable route in which the reaction is carried out under mild conditions and water is only one byproduct [4–7].

Titanium silicalite (TS-1) catalyst has been extensively investigated for the direct epoxidation because of high selectivity to propene oxide and high hydrogen peroxide conversion since Clerici and co-workers first demonstrated that TS-1 can be used efficiently as a catalyst for the epoxidation of various olefins [8–10]. Finally, the first commercial-scale propene oxide plant based upon the HPPO technology was built by Evonik and SKC in South Korea in 2008 [5]. In the Evonik–Uhde process, the highly exothermic epoxidation reaction is carried out in a specific fixed-bed reactor featured with high heat removal efficiency [11]. However, it is still highly necessary to develop a more efficient reactor concept employing catalyst immobilization that allows to eliminate the separation of nano-scaled TS-1 particles from it reaction liquid, enhance the stability of reactor operation and improve the economic feasibility of the process.

Several conventional types of reactor such as slurry, packed-bed and fluidized-bed reactor have been employed dominantly for catalytic gas-liquid-solid reactions in the chemical and petrochemical industry. Nevertheless, monolith reactors have drawn an increasing particular interest as a promising alternative since the use of structured packing, called "monolith", is expected to overcome the limitations and drawbacks of conventional reactors [12–16]. A monolith consists of a bundle of narrow parallel channels in which catalyst materials are impregnated

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Nomenclature

C_0, C_1	Constants [-]
Ca	Capillary number ($\mu_L U_{TB}/\sigma_L$) [-]
D_t	Tube diameter [m]
$E_\ddot{o}$	Eötvös number (($\rho_L - \rho_G)gD_t^2/\sigma_L$) [-]
g	Gravitational acceleration [m/s^2]
L_{LS}	Liquid slug length [m]
L_{TB}	Taylor bubble length [m]
Q_G	Gas flow rate [mL/min]
Q_L	Liquid flow rate [mL/min]
U_{LS}	Liquid slug rise velocity [m/s]

V_{GL}	Two-phase superficial velocity ($V_G + V_L$) [m/s]
U_{TB}	Taylor bubble rise velocity [m/s]
V_G	Gas superficial velocity [m/s]
V_L	Liquid superficial velocity [m/s]

Greek letters

ε	Gas injection ratio ($V_G/(V_G + V_L)$) [-]
ρ_G	Gas density [kg/m^3]
ρ_L	Liquid density [kg/m^3]
μ_L	Liquid viscosity [Pa s]
σ_L	Liquid surface tension [N/m]

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on or inside the walls. Its regular structure provides lower pressure drop, enhanced mass and heat transfer efficiency and ease of scale-up. Also, the separation of catalyst from product chemicals is unnecessary. However, in the gas-liquid monolith reactor, particularly at large scale, the maldistribution of gas and liquid over the multiple channels is a challenging issue due to its detrimental impact on the reactor performance [17]. Therefore, many researchers have investigated the flow distribution characteristics and examined various distributors to achieve a homogeneous distribution of gas and liquid [18–21].

In a multiphase monolith reactor, it is important to properly adopt a flow configuration and a hydrodynamic regime according to the relative flow rates of gas and liquid phase as these aspects significantly affect the reactor performance [22,23]. Among various patterns, due to the high mass-transfer rate between phases, special attention has been paid to slug flow or Taylor flow regime, in which gas bubbles and liquid slugs move consecutively through the monolith channel [24,25,15]. Vaitsis and colleagues suggested a novel design of monolith reactor, the confined slug flow (CSF) reactor, in which a rod was attached to the inner wall of monolith channel. They attained a slug flow regime with the catalyst insert inside a capillary and claimed that it opened the possibility of employing catalyst rods in monolith blocks [26].

As to the catalytic epoxidation of propene with hydrogen peroxide and TS-1 using methanol/water mixture, a number of papers have been published but most prior studies have been conducted in autoclave reactors. Only a limited number of researchers studied the propene epoxidation in gas-lift loop reactors or continuous flow fixed-bed reactors [27–33]. Thus, we scrutinized a confined Taylor flow (CTF) reactor as a unique reactor concept in one of our previous papers [34]. The aim of this paper is to advance the understanding of such structured reactors as conventional monolith and CTF reactor by comparing their hydrodynamic aspects and catalytic performances at atmospheric and high pressure. The hydrodynamic properties such as Taylor bubble length, bubble rise velocity, liquid slug length and slug rise velocity with respect to gas and liquid flow rate were investigated under Taylor flow regime.

The monolith and CTF reactor had different reactor column structures and showed very different hydrodynamic properties which in turn led to distinct performances for propene epoxidation. High operating pressure was observed to have a considerable influence on the hydrodynamics, in particular Taylor bubble length, and the propene oxide production rate increased in proportion to the operating pressure.

2. Material and methods

2.1. Catalyst preparation

TS-1 catalyst was synthesized on the basis of the method descried in the original patent by Taramasso and co-workers [35]. A solution of 1.5 g of tetraethyl orthotitanate (Sigma-Aldrich) was gradually added to 45 g of tetraethyl orthosilicate (Merck) with magnetic stirring for 30 min 100 g of 20 wt% tetrapropylammonium hydroxide solution

(Merck) was then gradually added to the mixed solution under stirring for an additional 30 min. After keeping the mixture at 60 °C for 3 h, 56 g of deionized water was added to the solution. The composition of the final solution was the same as the molar reagent ratios employed by Clerici et al. [9] The resulting solution was transferred to an autoclave in an oven and crystallized at 175 °C for 48 h without stirring. After cooling the solution to room temperature, the crystalline product was separated by centrifugation, followed by washing with deionized water. The step of washing and separation was repeated five times. The solid product was dried at 100 °C for 2 h and then finally calcined at 550 °C for 5 h in an air-atmosphere furnace. The resulting catalyst lump was ground into a powder using a pestle and mortar.

For its application to monolith and CTF reactor, the TS-1 catalyst prepared was immobilized on the inner wall of 500 mm long alumina tubes with 8 mm inner diameter (Multi-lab) and on the surface of 500 mm long alumina rods with 4 mm diameter (Multi-lab). Silica nanoparticles in the range of 10–50 nm (LUDOX® AS-40 colloidal silica, Sigma-Aldrich) were used together in order to enhance the mechanical strength of the catalyst coating because it was impossible to make a stable coating using TS-1 particles only. The silica nanoparticles with smaller size helped TS-1 particles with larger size get stuck not only on the alumina surface but also on other TS-1 particles.

For CTF reactor, a rod was dipped in a slurry of 20 wt% TS-1 and 15 wt% silica in deionized water. When the weight percent of silica in the slurry was less than 15 wt%, the durability of coating was reduced, on the other hand, when it was greater than 15 wt%, the activity of catalyst coating was likely to decrease because the active surface of TS-1 was covered excessively by inert silica nanoparticles. To get a predetermined weight of coating (1 ± 0.01 g), drying and dipping were repeated about 10 times. During the last repetitions, when a tiny amount of coating needed to be added to minimize the deviation from the predetermined weight, further diluted slurries, but still with the same ratio of TS-1 to silica, were used. In this case, the catalyst loading will be indicated as 2.0 g/m as the length of the rod is 0.5 m.

Similar procedures were employed to immobilize TS-1 catalyst on the inner surface of alumina tube for monolith reactor. Approximately 4 mL of a solution of 20 wt% TS-1 and 15 wt% silica in deionized water was injected into an alumina tube and the both sides of the tube were closed. Then, the tube was shaken many times to make the whole inner surface wet. The remaining catalyst solution was drained from the tube and the tube was dried. Drying and coating were repeated about 10 times to get a predetermined weight of coating (1 ± 0.01 g).

2.2. Epoxidation of propene

A 500 mm long alumina tube with TS-1 coating on the inner wall was used as a monolith reactor. The CTF reactor consisted of a 500 mm transparent polycarbonate tube (Cole-Parmer) and an alumina rod coated with TS-1 catalyst that was positioned axis-symmetrically in the reactor tube. For clarity, in this paper, the term "CTF reactor" is used when a rod is contained in the middle of reactor column, while the term