Catalytic micro-monolith reactor for continuous selective oxidation of methane

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Highlights

- High throughput 6-channel micro-monolith coated with ZSM-5 catalyst.
- A thin catalyst layer less than 5μ favours production of methanol.
- Over 80% methanol selectivity can be achieved at optimal conditions.

1. Introduction

The direct oxidation of methane to methanol is challenging, due to the inertness of methane, the low solubility of methane in aqueous solution, and the further oxidation of methanol [1]. Many studies of direct methane oxidation to methanol have focused on developing catalysts with testing in batch reactors [2]. Continuous reaction systems have lacked study and innovation. The micro-monolith membrane reactor operated as an interface contactor has significant advantages for process intensification, which include high mass and heat transfer, low pressure drop and safe operation. In this study, a 6-channel catalytic micro-monolith membrane reactor coated with catalysts was designed and constructed in a shell-tube configuration for the selective oxidation of methane with hydrogen peroxide.

2. Methods

The 6-channel micro-monolith was fabricated with 5mol% yttria-stabilized zirconia (YSZ) by the phase inversion and sintering method [3]. About 20mg ZSM-5 catalyst was coated uniformly inside each channel by the dip-coating method, followed by calcination at 550 °C to activate the catalyst and enhance the bonding to the monolith. The morphology of micro-monolith and the thickness of catalyst layer were analysed by scanning electron microscope (SEM).

The micro-monolith reactor was set up in a shell and tube configuration, where gas and liquid reactants were fed to the shell and tube side of the monolith, respectively, as shown in Figure 1b. In a typical reaction, 0.5M H_2O_2 solution was pumped through the tube side at 0.5ml/min, which was directly contacted with ZSM-5 catalyst. CH_4 reactant gas was pressurised in the shell side of the monolith and reached the catalyst layer through the porous wall of the micro-monolith. The reaction was conducted at 50 °C, 1 bar gas pressure.

The liquid products were analysed by a Bruker AVANCE III 400 NMR spectrometer. The concentration of H_2O_2 was analysed by titration.

3. Results and discussion

The 6-channel micro monolith, as shown in Figure 1a, was successfully fabricated with an average channel diameter of 0.8mm and an overall outer diameter of 2.7mm, providing a high surface area per volume of around 5000 m^2/m^3. The thickness of ZSM-5 catalyst layer with various catalyst amounts was analysed by SEM, and the catalytic performance is shown in Figure 1c. Increasing the overall amount of the catalyst and the thickness of the catalyst layer firstly enhanced the production of formic acid and reached a plateau, while the production of methanol gradually decreased. The selectivity to formic acid increased from around 40% to 84%. This result indicates that the addition catalyst layer mainly benefits the overoxidation of methanol to formic acid. To tune product selectivity towards methanol, several reaction parameters, including H_2O_2 concentration, liquid flow rate, and operation pressure, were studied.

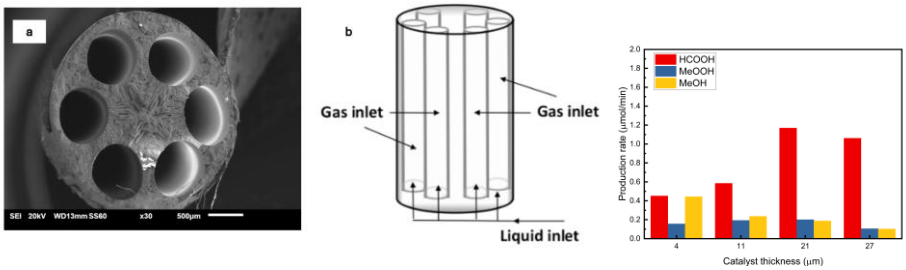

Figure 1. Micro-monolith reactor: (a) SEM image of 6-channel micro-monolith cross-section; (b) membrane reactor; (c) production rate for 5mg to 40mg ZSM-5 catalyst.

4. Conclusions

Direct selective oxidation of methane by H2O2 was operated continuously in a 6-channel micro-monolith reactor which acted as an interface contactor. The thickness of the catalyst layer significantly controlled the product distribution, where the thicker catalyst layer promoted overoxidation of methanol to formic acid. A thin catalyst layer of around 5μm was found optimal for achieving a high selectivity to methanol. By optimising reaction parameters, the selectivity of methanol can achieve 80% [4].

References

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Keywords

Catalytic membrane reactor; ceramic micro-monolith; direct oxidation of methane to methanol.