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3D microstructured reactor for iron-based catalytic selective oxidation of benzyl alcohol into benzaldehyde in continuous flow reactor

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1. Introduction

There is an ongoing search in the chemical industry for ways of improving continuous processes in terms of intensification, sustainability, and economic profitability. A promising approach is the development of novel and tailored, porous catalyst bed architectures and their optimal integration into continuous flow reactors. These novel architectures are micro-structured catalytic beds developed by a direct write or 3D fibre deposition (also referred to as microextrusion) (3DFD)[1], [2]. The novel catalyst structures combine the major advantages of a low-pressure drop, good mass- and heat transfer, good mixing, high surface area and a reactor framework directly made of the catalytic material. While these 3D microstructured reactors are already being used in catalytic continuous flow processes in the gaseous phase[3], newly developed formulations and well-defined geometries are a competitive alternative to the conventional packed bed/bath reactors in three-phase processes (involving solid catalyst, liquid, and gaseous reactants). The selective oxidation of benzyl alcohol (BA) into benzaldehyde (BZ) is well-referenced for common multiphase heterogeneous catalysis over various metals or supports, predominantly in batch systems [4], [5] and less commonly in lab-scale continuous systems [6], [7]. This study intends to demonstrate the viability of 3Dmicrostructured reactors for aerobic selective oxidation of BA into BZ by using lower content in rare metal catalysts and platinum-group metals such as palladium, which can be partially replaced by less active but more sustainable metals such as cobalt or even iron.

2. Methods

Figure 1 3D-Printing of the microstructured reactor by paste extrusion of Fe15Co15@Al2O3

Solid γ-Al_2O_3 powder support (Puralox TH 100/150, Sasol) was functionalised by iron, cobalt and palladium precursors have via wet impregnation. The as-synthetised catalysts $Fe_xM_y@Al_2O_3$ (M=Co or Pd) are dried and mixed with binders with homemade formulations leading to a highly viscous paste suitable for 3D printing. The manufacturing of 3D microstructures is carried out by the extrusion of the viscous paste through a thin nozzle mounted on a CNC (computer numerical control) machine and x,y,z-table. Typical structures in this study were built layer-by-layer into cylinders of 25mm diameter and 30mm high, while the extrusion fibre diameter and interfibre distance are 800µm (Figure 1). Two different internal geometries are explored, in 1-1 stacking with each layer rotated at 90° from the previous one and in 1-3 stacking with each layer rotated at 90° from the previous one and translated at a step size of the fibre diameter, 800µm. Once printed, the 3Dmicrostructures are employed as monoliths in a continuous flow column reactor, firstly for calcination and activation at a temperature of 500°C and diluted O_2 in He in order to remove organic binders from the formulation, and afterwards, for reduction under H_2.

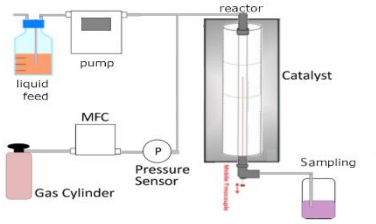

Figure 2 Lab set-up of the gravimetric column as continuous flow reactor for 3D-microstructured reactors

The reactor is fed by pumping a flow of 0.1mL.min^{-1} of 0.2mol.L^{-1} BA in DMF solution under a counter current controlled airflow of 85mL.min^{-1} and at a temperature of 100°C and 1atm, as presented in Figure 2. The product samples are obtained at the bottom of the column after 4h.

3. Results and discussion

In comparison to a batch reactor system, the microstructured catalytic materials with the same loading of iron and palladium in the 3Dcontinuous flow reactor exhibited equally high catalytic activity with conversion rates of over 80% and Turn Over frequency (TOF) of over 0.04h^{-1}. The structured catalysts show higher conversion and TOF than a conventional packed bed, revealing the impact of the new design which offer better control of the process and surface area of contact between the catalytic material and solution feeding. However, the catalytic conversion of BA occurring at high frequency on the entire length of the structure over very active palladium leads to lower selectivity into BZ than in batch. An advantageous solution to increase selectivity is the replacement of palladium by cobalt as an alternative catalytic material proposing the same selective conversion at lower cost.

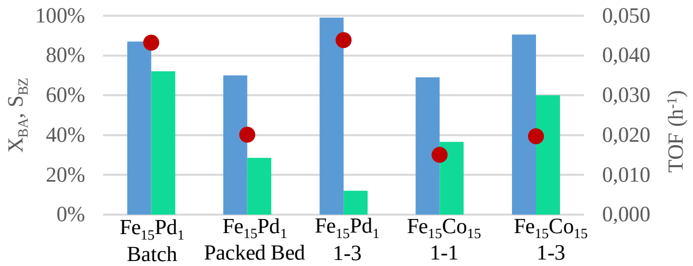

Figure 3 Catalytic performance observed. Reaction conditions described in methods. Keys: Left bars show the conversion of X_{BA}(■) and right bars the selectivity S_{BZ}(■) in %. The turn over frequency TOF (●) is expressed in h^{-1}.

4. Conclusions

3D-Microstructured reactors provide a sustainable solution for multiphase heterogeneous catalysis such as selective oxidation of BA to BZ, offering a commercially viable alternative to batch system or PGM metals replacement.

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