



## Continuously operated falling film microreactor for selective hydrogenation of carbon–carbon triple bonds



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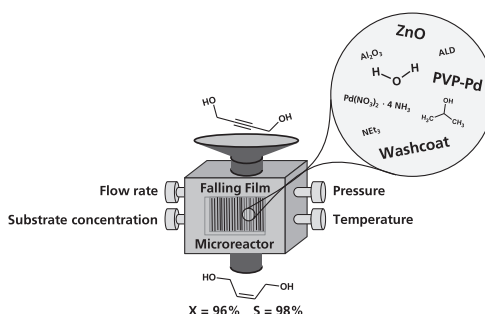
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### HIGHLIGHTS

- Process intensification with microstructured reactor equipment.
- Continuous-flow gas–liquid–solid reaction.
- Novel catalyst development with atomic layer deposition and PVP-Pd NPs.
- Water as selectivity-enhancing and environmental friendly solvent.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Despite significant advances in the fabrication and applications of microreactors for production of chemicals, their use for catalytic reactions remains a challenge, especially in fine chemical synthesis where the selectivity towards the desired product is an issue. A falling film microstructured reactor (FFMR) was tested in the selective hydrogenation of 2-butyne-1,4-diol (**1**) to its olefinic derivative (**2**). The FFMR plates were coated with  $\text{Al}_2\text{O}_3$  or ZnO followed by the deposition of Pd nanoparticles (NPs). The oxides were deposited on the microstructured reaction plates using either conventional washcoating or atomic layer deposition (ALD) in the liquid or gas phase, respectively. The Pd-NPs were either formed via impregnation of an organometallic precursor with subsequent reduction, or with pre-fabricated Pd-NPs stabilized in poly(vinyl pyrrolidone) (PVP) with subsequent pyrolysis of the organic matrix and activation in  $\text{H}_2$  atmosphere. The palladium loading was varied in the range of 1.1–13.6 wt%. Different solvents including water, 2-propanol and mixtures with organic bases were tested aiming at their environmental impact and highest activity/selectivity. In this work the best performing catalyst was 1.1 wt% of Pd on ZnO which was prepared by washcoating and pre-fabricated Pd NPs. Under optimized conditions with water as solvent 98% of selectivity at 96% conversion was obtained, which was close to the results of the benchmark reaction in batch mode (with 98% selectivity at 99% conversion). Finally, the FFMR demonstrated a 15-fold higher performance in comparison with a batch-operated reactor showing important process intensification for the hydrogenation of (**1**) to (**2**) in continuous-flow mode.

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## 1. Introduction

Despite significant advances in the fabrication and applications of microreactors for production of chemicals, their use for catalytic reactions remains a challenge, especially in fine chemical synthesis where the selectivity towards the desired product is an issue. Acetylene diols are frequently used precursor molecules in industrially relevant reactions. For example, the selective hydrogenation of the C–C triple bond in 2-butyne-1,4-diol (**1**) is an important process in fine chemical synthesis since the olefinic product 2-butene-1,4-diol (**2**) is a valuable precursor molecule in the synthesis of pharmaceuticals like vitamins A and B6, or insecticides like endosulfan [1–3]. Hence, several catalytic systems have been developed for this reaction using Pt [4,5], Pd [6–8] or Pd-based bimetallic catalysts [9] combined with various stabilizers like polymers [10] and block-copolymers [11] or supports like filamentous active carbon [12,13] or layered double hydroxides [14]. Recently bacteria biomass supports were used by generating Pd active phase on bacteria cell walls [15]. The catalysts described above were used either in batch mode or in (looped) continuous mode using different reactor types like trickle-bed or single-capillary reactors.

Falling film reactors are another reactor type suitable for gas/liquid (g/l)-reactions. Thin liquid films with a thickness of 0.5–3 mm can be generated by pulling down a liquid on the reactor surface via gravitational forces [16,17]. In consequence to the low film thickness, heat and mass transfer is rapid. For achieving even thinner films with a high interfacial area between the gas and liquid phase a microstructured falling film reactor (FFMR, Fig. 1) was developed allowing film thicknesses below 100  $\mu\text{m}$  [18–26]. The reaction plates with microchannels of various depth and width are the key elements of this reactor type (e.g. 1200  $\mu\text{m}$   $\times$  400  $\mu\text{m}$ , 600  $\mu\text{m}$   $\times$  200  $\mu\text{m}$ , 300  $\mu\text{m}$   $\times$  100  $\mu\text{m}$ ; channel length 78 mm). In addition to the gravitational forces capillary forces stabilize the liquid thin film in the microchannels for efficient g/l-contact.

For g/l/solid (g/l/s)-reactions FFMRs have only rarely been used so far, although the exchangeable reaction plates can be coated by different catalysts and can be easily adapted for a particular reaction. This approach presents a valuable option for selective hydrogenations in flow mode. Beside the hydrogenation of  $\alpha$ -methylstyrene [27], the highly exothermic transformation of nitrobenzene to aniline [28] demonstrated the excellent heat removal capability of the FFMR. First detailed studies on the flow behavior with particular mass transfer properties were performed with a plate having medium sized microchannels (600  $\mu\text{m}$   $\times$  200  $\mu\text{m}$ ). Here the hydrogenation of  $\alpha$ -methylstyrene with 5 wt% Pd on  $\text{Al}_2\text{O}_3$  is one rare example for a g/l/s-reaction in a FFMR [29].

The goal of this work was to broaden the number of catalytically active materials varying support coatings which can be adapted for

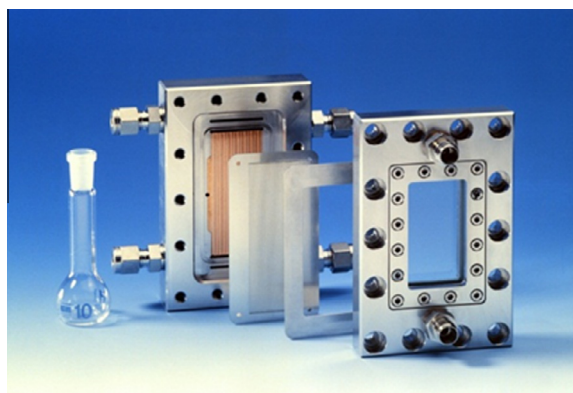


Fig. 1. Disassembled FFMR with the reaction plate as key element close to the heat exchanger structure in the bottom plate of the reactor (© Fraunhofer ICT-IMM).

multiple selective hydrogenation reactions of industrial relevance. The selective hydrogenation of the C–C triple bond in (**1**) rendering exclusively (**2**) was taken as a model reaction due to its industrial importance.

## 2. Experimental

### 2.1. Catalytic hydrogenation reaction

The selective hydrogenation of acetylenic diol (**1**) to (**2**) comprises a complex reaction network including also a full hydrogenation to butane-1,4-diol (**3**) as a main by-product, which is the starting material for the acid-catalyzed synthesis of tetrahydrofuran. Depending on the catalyst and the reaction conditions further transformations are possible resulting in  $\gamma$ -hydroxy butyraldehyde (**4**), crotyl alcohol (**5**), *n*-butanol (**6**), *n*-butylaldehyde (**7**) and 2-hydroxy tetrahydrofuran (**8**). All reaction pathways are well-documented in the literature giving a solid base for optimized benchmark catalytic systems and reaction conditions (Fig. 2) [6,7,13,15].

The substrate 2-butyne-1,4-diol (**1**, ALDRICH, 99% or MERCK, >99%) was used as received without further purification. As main solvents 2-propanol (SIGMA–ALDRICH, 99.7%) and deionized water (MERCK Millipore Milli-Q Plus Water Purification System) were used. As co-solvents, pyridine (SIGMA–ALDRICH, 99+% ACS), piperidine (ALFA AESAR, 99%) and triethylamine (CARL ROTH, 99.5%) were used as received.

### 2.2. Catalyst preparation and immobilization on microreactor plates

#### 2.2.1. Microreactor plates

Microstructured plates made of stainless steel (FRAUNHOFER ICT-IMM) were used with a channel architecture of 600  $\mu\text{m}$  in width and 200  $\mu\text{m}$  in depth (32 channels/plate) in all experiments, except for reaction plate P4 a channel architecture of 1200  $\mu\text{m}$   $\times$  400  $\mu\text{m}$  was used (16 channels/plate).

#### 2.2.2. Method A: Slurry/washcoating process for the deposition of support material followed by Pd precursor incipient wetness impregnation

2.2.2.1. Deposition of support. The liquid-phase preparation of ZnO and  $\text{Al}_2\text{O}_3$  washcoats was done according to literature procedures [30,31]. The method is exemplified here for ZnO. 2.5 g of poly(vinyl alcohol) (PVA) used as a binder (SIGMA ALDRICH, Mowiol 40-88) were mixed with 42.5  $\text{cm}^3$  of distilled water and stirred at 338 K for 2–3 h. 5 g of ZnO (SIGMA ALDRICH, 255750) and 0.375 g concentrated acetic acid were added to the solution and stirred for

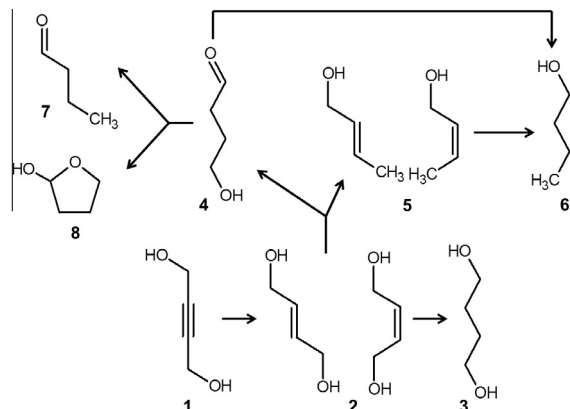


Fig. 2. Complex reaction network of the catalytic hydrogenation of 2-butyne-1,4-diol [6,7,13,15].

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