

# A 'PLUG & PLAY' MICRO REACTOR FOR RAPID SCREENING OF THE ACTIVITY OF A CATALYST ON DIFFERENT SUPPORTS

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## Summary

A 'plug & play' micro reactor is demonstrated for the rapid screening of the activity of a heterogeneous catalyst on different types of supports. The micro reactor can hold three interchangeable plates with each the same catalyst support. As a proof-of-principle, the hydrogenation of 3-methyl-1-pentyn-3-ol over a Pd catalyst has been performed over three different supports, viz., flat plates, washcoated plates and plates covered with carbon nano fibres. The flat plate support shows (partly) kinetically limited reaction rates, where carbon nano fibres do not run into these limitations, due to the larger surface area available for catalyst deposition.

## Keywords

Micro Reactor, Catalyst Support, Hydrogenation Reaction

## Introduction

The small sub-millimeter dimensions and large surface-to-volume ratios of micro reactors provide important advantages over conventional larger reactors. For example, mass and heat transfer rates are high and hot spot formation is easily prevented. Because of the relatively high rates of mass transfer in micro reactors, usually both intrinsic kinetics and mass transfer contribute to the overall rate of reaction. Most often, therefore, the rate of production will increase when a larger catalytic surface area is available in the reactor, provided that the catalyst remains fully accessible. Larger surface areas per unit of reactor volume can be obtained by applying supports on which the catalyst is deposited.

These supports are for example small particles in micro packed-beds<sup>1,2</sup>, wash coats on micro channel walls<sup>3,4</sup>, zeolites deposited on micro platelets<sup>5</sup>, or carbon nano fibres<sup>6</sup> coated on micro channel or capillary walls. However, the conditions of the production processes of these supports and the catalyst can be too harsh to be performed 'on board' in the micro reactor. Therefore, in this work, a 'plug & play' micro reactor, where the surface enlarging support with catalyst can be easily exchanged, is introduced and demonstrated.

## Experimental

The reactor consists of a channel having a length of 156 mm, a width of 5 mm and a depth of 500  $\mu\text{m}$ , where gas

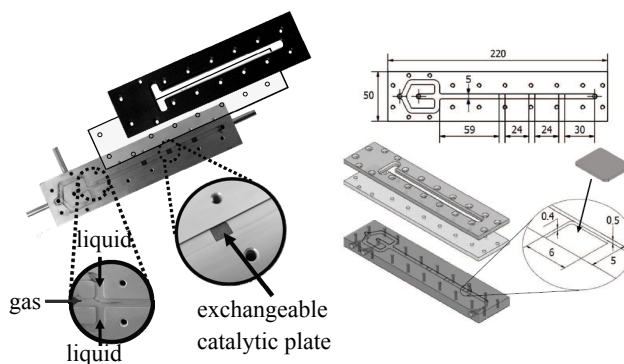


Figure 1: 'Plug & play' micro reactor with three catalytic plates inserted in the micro channel. Gas and liquid phase reactants are fed cross-currently at the micro channel inlet.

and liquid are fed cross-currently to the channel inlet (Figure 1). The reactor is designed to contain three individual plates with each a width of 5 mm, a length of 6 mm and a thickness of 0.36 mm. The plates are placed consecutively in the channel with a spacing of 24 mm to regain a fully developed flow between two consecutive plates. Since the top of the reactor can be taken off, the plates can be easily removed and replaced within ten minutes by plates which can be prepared off-line.

A proof-of-principle study of the screening of a catalyst on different supports was performed using the selective hydrogenation of 3-methyl-1-pentyn-3-ol (Figure 2) in ethanol over Pd as catalyst deposited on flat plates, wash coated plates, and on plates on which carbon nano

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fibres have been grown with different fiber thicknesses (325, 29, and 62 nm) and lengths (5, 2.2, and 7.3  $\mu\text{m}$ ).

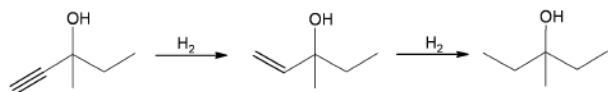


Figure 2: Hydrogenation reaction of 3-methyl-1-pentyn-3-ol to the desired 3-methyl-1-penten-3-ol and the undesired second hydrogenation to 3-methyl-1-pentanol.

The hydrogenation reaction was performed for the case of liquid flow only with hydrogen dissolved in the liquid, and for the case of gas-liquid flow with separate inlets of gas and liquid. The product outlet concentration was measured with a GC at hydrogen flows from 0 to 1 m/s and liquid flows of  $5 \times 10^{-3}$  to 0.167 m/s. The reaction temperature was varied from 295 to 338 K.

## Results

The hydrogen conversion is presented in Figure 3a as a function of the liquid residence time. The hydrogen conversion in the case of the plates with carbon nano fibres with an average fiber thickness of 62 nm and a layer thickness of 7.3  $\mu\text{m}$  is increased with a factor of two compared with the flat plates for similar liquid residence times (Figure 3a). Both catalyst supports achieved 100% selectivity towards 3-methyl-1-penten-3-ol at all temperatures and liquid residence times.

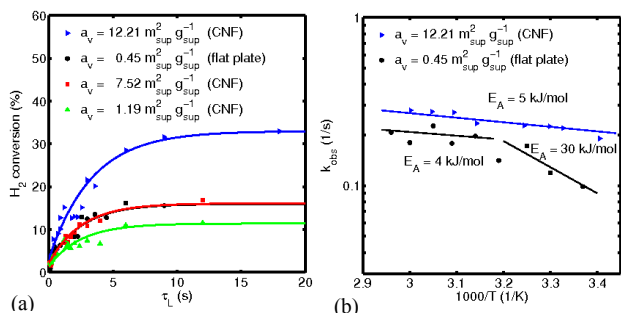


Figure 3: The liquid-phase hydrogenation of 3-methyl-1-pentyn-3-ol over the different catalyst supports with 0.04 wt-% Pd on carbon: (a) hydrogen conversion as a function of the liquid residence time at 298 K; (b) Arrhenius plot for  $u_{L,s}^0 = 0.05 \text{ m s}^{-1}$ .

Arrhenius plots show that for flat plates both external mass transfer ( $E_A \approx 4\text{--}5 \text{ kJ/mole}$ ) and intrinsic kinetics ( $E_A \approx 30 \text{ kJ/mole}$ ) contribute to the overall reaction rate depending on the reaction temperature chosen. However, for carbon nano fibres, kinetic limitations do not play a role and only external mass transfer limitations are observed (Figure 3b). This is due to the increase in surface area available for catalyst deposition.

A flow map of the different observed flow regimes was made for the alkyne in ethanol solution and gaseous hydrogen over the different catalyst supports (Figure 4). Mass transfer rates, conversions and selectivities were determined at different liquid and gas velocities ( $Re_L = 6 \times 10^{-3}$  to 25,  $Re_G = 0.34$  to 8.5). More results will be given in the paper.

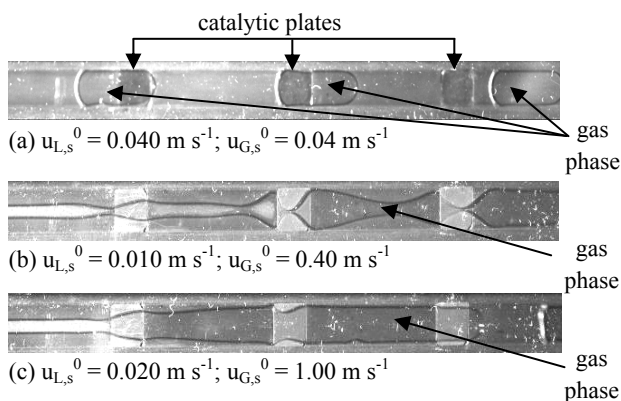


Figure 4: Flow patterns of liquid 3-methyl-1-pentyn-3-ol in ethanol and gaseous  $\text{H}_2$  in a  $500 \times 5000 \mu\text{m}$  rectangular micro channel with three exchangeable plates covered with carbon nano fibres on which Pd is deposited: (a) Taylor flow; (b) ring/annular flow; (c) annular flow.

## Conclusions

A 'plug & play' micro reactor has been presented that proves to be a practical tool for rapid catalyst testing and screening, where the catalyst can be prepared outside the micro channel and replaced within minutes. With the proof-of-principle study of the hydrogenation of 3-methyl-1-pentyn-3-ol over Pd, it was proven that carbon nano fibers as a catalyst support overcome kinetic limitations due to a larger surface area compared with flat plates. Therefore, an increase in conversion of a factor of two was observed for the carbon nano fibers compared with flat plates at similar liquid residence times.

## References

- (1) Kiwi-Minsker, L.; Renken, A. Microstructured reactors for catalytic reactions. *Catalysis Today* **2005**, 110, 2-14.
- (2) Losey, M. W.; Schmidt, M. A.; Jensen, K. F. Microfabricated multiphase packed-bed reactors: Characterization of mass transfer and reactions. *Industrial & Engineering Chemistry Research* **2001**, 40, 2555-2562.
- (3) Nijhuis, T. A.; Kreutzer, M. T.; Romijn, A. C. J.; Kapteijn, F.; Moulijn, J. A. Monolithic catalysts as more efficient three-phase reactors. *Catalysis Today* **2001**, 66, 157-165.
- (4) Degenstein, N. J.; Subramanian, R.; Schmidt, L. D. Partial oxidation of n-hexadecane at short contact times: Catalyst and washcoat loading and catalyst morphology. *Applied Catalysis A* **2006**, 3005, 146-159.
- (5) Mies, M. J. M.; van den Bosch, J. L. P.; Rebrov, E. V.; Jansen, J. C.; de Croon, M. H. J. M.; Schouten, J. C. Hydrothermal synthesis and characterization of ZSM-5 coatings on a molybdenum support and scale-up for application in microreactors. *Catalysis Today* **2005**, 110, 38-46.
- (6) Thakur, D. B.; Tiggelaar, R. M.; Seshan, K.; Gardeniers, J. G. E.; Lefferts, L. Synthesis of carbon nanofibers as support layer for metal catalyst in a microreactor for three-phase reactions. *Advances Sciences Technologies*, **2006**, 54, 231-236.