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# Specificities of micro-structured reactors for hydrogen production and purification

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**Abstract**

This paper presents the specificities of micro-structured reactors as compared to conventional fixed-bed reactors through two case studies devoted to (i) hydrogen production by methanol steam reforming, (ii) hydrogen purification by water-gas shift (WGS). Key features like catalyst coating stability, temperature and pressure management, effects of operating conditions (residence time, pressure drops, etc.) are well identified as controlling the micro-reactor performances for methanol reforming. These devices are also shown to be excellent tools for fast access to reaction kinetics as exemplified for the WGS reaction, subject to operating conditions carefully chosen to ensure proper hydrodynamics, in order to use conventional plug flow reactor models for extracting rate constants.


*Keywords:* Methanol reforming; Water-gas shift; Micro-reactors; Kinetics

## 1. Introduction

Sustainable chemistry and exploitation of energy sources for the next decades requires considerable progress in process intensification. A development of new tools and equipments meeting the objectives of high efficiency, improved safety, compactness and low implementation costs is therefore subject of intensive research effort. Among the various scenarios tested in R&D, micro-structured reactors appear as a highly promising technology [1] and perspectives of mass production are already announced by technology providers [2]. These reactors are based on assembly/stacking of micro-structured plates or fibres. Due to their high heat and/or mass transfer, low pressure drop and good phase contacting, they seem particularly adapted to the large domain of hydrogen production by fuel reforming and purification. However, specificities for catalyst washcoating, platelets assembly and operating conditions have to be carefully considered for implementing correctly these new structured reactors. This paper presents some of these features characteristic of micro-reactors through two case studies dedicated to hydrogen production and purification for feeding fuel cells: (i) comparison between fixed-bed and micro-structured reactor for the reforming of methanol into hydrogen and carbon oxides and (ii) use of micro-structured reactors in kinetic studies on the water-gas shift (WGS) reaction.

## 2. Case study 1: methanol steam reforming

The recovery of chemically stored hydrogen by methanol steam reforming can be considered as an alternative to cryogenic or pressurised hydrogen storage. Though large efforts of catalysts development exist for this reaction, still few studies consider this application in micro-structured reactors.

### 2.1. Catalyst

A Cu/Zn/Al powder catalyst, namely G-66MR supplied by Süd-Chemie, was tested either in a fixed-bed reactor or in a micro-structured reactor consisting of stacked coated micro-channels sheets. In both cases, the catalysts were pre-reduced

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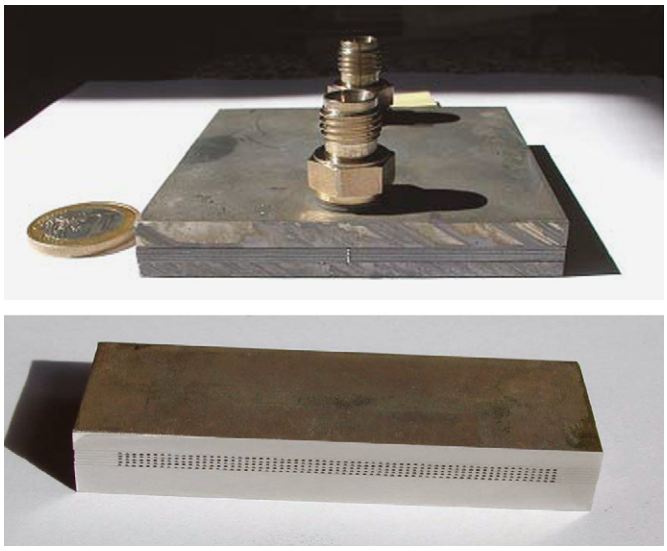

Fig. 1. Micro-structured reactor views for performances tests (external and cross-section cut views).

(ramp to 513 K at 4 K/min with 10% $H_2$ in $N_2$, then stay at 513 K for 30 min and decrease to operating temperature) and the water-to-methanol ratio remained unchanged during all experiments ($H_2O$/MeOH = 1), fixing the respective molar fractions typically to 33%. Micro-structured reactors contained the catalyst on five sheets made of $AlMg_3$ with 63 channels each, having a width of 0.5 mm, a depth of 0.23 mm and a length of 59 mm. The platelets were structured by photochemical milling (PCM), i.e. wet chemical etching. The catalyst was coated on the platelet surface using a suspension obtained after intensive milling of the commercial catalyst, provided as 5 mm pellets diameter. The reactor was then assembled by integral soldering presenting a particularly safe technique to avoid any leaks. A global picture of the micro-structured reactor used and its cross-section view obtained by cutting perpendicular to the channel axis are depicted in Fig. 1. Conventional fixed-bed reference experiments were performed with a sieved fraction in the size range of 100–200 μm of pelletised catalyst, initially milled, put to suspension and dried like for the platelets coating.

### 2.2. Testing conditions

The potential of micro-structured reactions in process intensification relates to superior mass and heat transfer, being more reaction engineering parameters than materials properties of the catalyst. It is, therefore, indispensable to benchmark a micro-structured device against a conventional fixed-bed configuration in the absence of mass transfer limitations. Given the thin catalyst layer in the structured reactor and the relatively small particle size of 100–200 μm used in the fixed-bed configuration, mass transfer limitations by intraparticle diffusion are considered to be absent. Calculation of Weisz modulus confirms this hypothesis (efficiency factor close to 1.0 over the whole range of temperature). In order to establish the absence

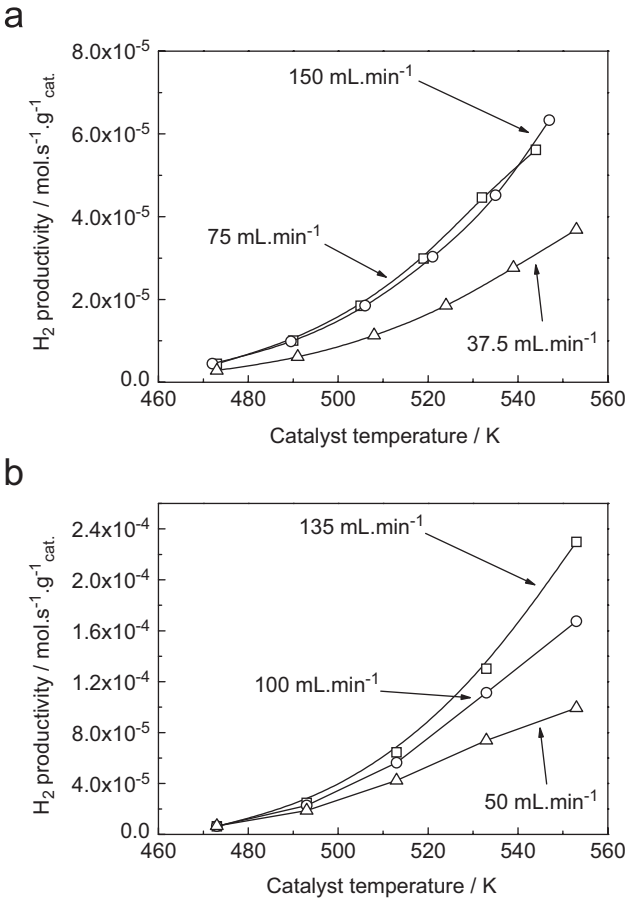


Fig. 2. (a) Hydrogen productivity versus reaction temperature in a fixed-bed reactor at feed rates of 37.5, 75 and 150 mL $min^{-1}$ using a catalyst loading of 199.5 mg. (b) Hydrogen productivity versus reaction temperature at feed rates of 50, 100 and 135 mL $min^{-1}$ in a micro-structured reactor containing 116 mg catalyst of five sheets with 63 channels each. Reactant composition: 33% $CH_3OH$, 33% $H_2O$, balanced by inert gas.

of limitations by extra particle diffusion, the hydrogen productivity was determined at different reactant flow rates. Fig. 2a depicts the hydrogen productivity at a feed flow of 37.5, 75.0 and 150.0 mL $min^{-1}$ as a function of the catalyst temperature (directly measured among the particles catalyst) for the fixed-bed configuration. The well matching of all productivities at flows of 75 and 150 mL $min^{-1}$ indicates that the steam reforming reaction is not limited by extra particle diffusion, while there is a significant limitation at lower flows. Respective results for the micro-structured reactor are presented in Fig. 2b for flows of 50, 100 and 135 mL $min^{-1}$. The increase of productivity with increasing reactant flow indicates that higher flow rates are required to avoid limitations by extra particle diffusion. In order to strengthen that at the highest tested flow of 135 mL $min^{-1}$ no mass transfer limitation prevails, the activation energy of the hydrogen formation were determined and compared to the values obtained with the same catalyst in the fixed-bed configuration. As outlined in Table 1, the activation energy value observed at 135 mL $min^{-1}$ corresponds well to those observed in fixed-bed operation without mass transfer limitation, while the decrease of the apparent activation energy at lower flow is characteristic