Preparation of Pt/ZSM-5 films on stainless steel microreactors

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Abstract

Different synthesis methods (seeded and unseeded liquid phase hydrothermal synthesis, steam-assisted crystallization) have been employed to prepare zeolite films as catalytic coatings on the channels of stainless steel microreactors. The best results were obtained using seeded steam-assisted crystallization (SAC) which under suitable conditions led to well-crystallized zeolite films whose growth was confined to the channel spaces. Liquid phase synthesis yielded higher catalyst loads but was less effective in confining crystal growth to the desired regions. Once the zeolite films were formed, conventional ion-exchange procedures were used to produce a homogeneous distribution of Pt in the zeolite films.
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1. Introduction

In recent years, microstructured reactors have become one of the most active research areas in catalysis and reaction engineering, as witnessed by several review papers on this subject [1–7]. Microstructured reactors are three-dimensional structures with inner dimensions measured in tens to hundreds of microns [5]. The main feature of microreactors is their high surface area to volume ratio, with values between 5000 and 50,000 $m^2\,m^{-3}$, while those of traditional reactors are about 100 $m^2\,m^{-3}$, reaching values of 1000 $m^2\,m^{-3}$ only in exceptional cases. The enhancement of transport properties in microreactors produces high heat transfer rates, allowing for instance to carry out highly exothermic reactions under near-isothermal conditions [8]. The avoidance of hot spots not only results in a safer operation, but also helps to suppress undesirable side reactions, leading to higher selectivity, yield, and product quality. In addition, mass transfer processes can also be accelerated considerably in microreactors because of their small dimensions. This means that it is possible to strongly reduce diffusion times in microreactors, thus reducing the mass-transfer limited operating region. Finally, process parameters such as pressure, temperature and residence time are more easily controlled in reactions that take place in small volumes. The potential hazard of strongly exothermic or explosive reactions could be drastically reduced and the same can be said of processes that operate with toxic substances or under high operating pressures, where a microreactor offers higher safety levels than conventional reactors [9].

The above mentioned properties also make microreactors suitable as process engineering tools for acquiring kinetic and design data useful for scaling up new processes and for the optimization of those already in operation [10]. Microreactors also give opportunities for new production concepts: depending on demand, several microreactors could be stacked in parallel to achieve the desired product output, thus achieving a flexible production capacity.

Catalytic activity has been introduced into microreactors by loading noble metals (e.g. Pt [11], Pd [12]) or mixtures of metals or metal oxides (e.g. [13–15]), normally as a washcoat with a suitable support on the microchannels. In this respect, zeolites are especially interesting candidates as catalyst supports, on account of their ability to grow as films on a variety of surfaces. In addition, the ion exchange capacity and the microporous structure of zeolites facilitate a homogeneous distribution of metal active sites. In spite of these properties, there are relatively few publications related to zeolite catalysts in microreactors.

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The group of Yeung has prepared zeolite microreactors consisting of zeolite synthesised over silicon wafers in which microchannels are made by means of photolithography [16,17]. In this way Ti-silicalite was synthesised over silicon wafers for their application on the epoxidation of 1-pentene [18,19]. They also studied membrane microreactors prepared in multichannel porous stainless steel plates where zeolite films play a separative role without catalytic activity, while the zeolite catalyst nanoparticles were coated on the microchanel [20–22].

The synthesis of zeolites on stainless steel microreactors was studied by Rebrov et al. [23]. They prepared ZSM-5 films over a stainless steel microreactor for the selective reduction of NO to NH_3 with a high yield of product. In addition, Mies et al. [24] investigated the synthesis of zeolite ZSM-5 on molybdenum plates and the scale-up of the synthesis process. They demonstrated a uniform coverage of $14.8 + 0.4$ g/m^2 on a set of 72 molybdenum plates.

Previous works in our laboratory have addressed the advantages of using zeolite films in micro-scale applications [25], including the advantages of coupling reaction and separation at the microscopic level [26]. We have also studied the preparation of zeolite films on a variety of supports, including metallic surfaces [27,28] and ceramic monoliths [29]. In this work, however, we have applied different techniques to optimize the synthesis of zeolite layers on the microchannels of stainless steel microreactors, with the aim of attaining a homogeneous zeolite coating while preserving a high degree of catalyst accessibility.

2. Experimental

2.1. Zeolite synthesis and characterization

Na-ZSM-5 has been prepared, both as powder and also as a film supported on stainless steel microreactors. The microreactors (see Fig. 1) consist of two Plates 50 mm long, 10 mm wide and with a thickness of 2 mm manufactured at Institut für Mikrotechnik Mainz (IMM). In each Plate 14 microchannels (length = 41 mm, diameter = 500 μm) are connected to wider inlet and outlet sections as shown in Fig. 1. Before synthesis the
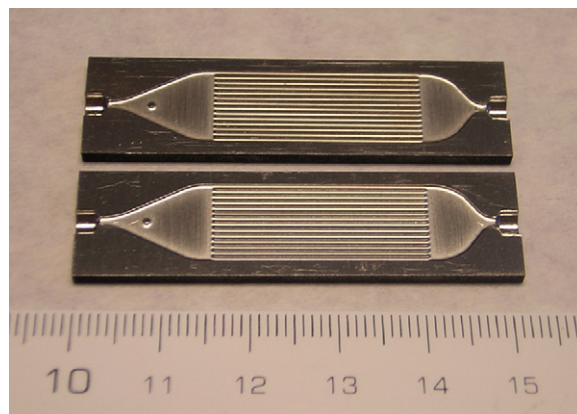

Fig. 1. Images of the starting stainless steel reactor plates showing the microchannels and the inlet/outer sections.

plates were subjected to a cleaning procedure using nitric acid (1 wt%) during 4 h at 60 °C. Afterwards the plates were thoroughly washed with distilled water and cleaned in an ultrasound bath with water and acetone alternatively, followed by drying at 100 °C.

Two different gel compositions were employed for the synthesis of Na-ZSM-5. In gel Z5-1 the molar composition was $21SiO_2:X \times 987H_2O:3NaOH:1TPAOH:0.105Al_2O_3$; with $X = 1$; a more diluted gel, Z5-2 (in which $X = 2$) was also employed to reduce homogeneous nucleation and growth of crystals in the bulk of the synthesis solution. The synthesis temperature was varied between 120 and 170 °C and three different synthesis methods were employed, namely, direct liquid phase hydrothermal synthesis, seeded liquid phase hydrothermal synthesis (LHS, also called secondary growth synthesis), and steam-assisted crystallization (SAC). Table 1 summarizes the conditions used during the synthesis of the Na-ZSM-5 films prepared in this work, as well as the zeolite weight gain after synthesis.

2.1.1. Liquid phase hydrothermal synthesis

The stainless steel plate was placed vertically (Fig. 2a) in a teflon-lined autoclave filled with gel Z5-1. The autoclave was placed in a stove and the hydrothermal synthesis was carried

Table 1
Synthesis conditions and weight gain for the zeolite-coated microreactors

Sample	Type of synthesis	Treatment of channel	Gel	Synthesis time	T [°C]	Zeolite gain [mg/g]
MR-1	LHS	None	Z5-1	8 h	170	2.65
MR-2	LHS	Acid	Z5-1	8 h	170	2.08
MR-3	LHS	Seeding	Z5-1	8 h	170	1.07
MR-4	LHS	Seeding	Z5-2	8 h	150	1.71[a]
MR-5	LHS	Seeding	Z5-2	8 h	120	0.43[a]
MR-6	LHS	Seeding	Z5-1	8 h	170	1.14
MR-7	LHS-closed	Seeding	Z5-2	8h + 15 h	150	1.06
MR-8	LHS-closed	Seeding	Z5-2	8h + 15 h	150	0.83
MR-9	SAC	None	Z5-1	4 d	170	0.69[a]
MR-10	SAC	Seeding	Z5-2	8 d	170	0.22[a]
MR-11	SAC	Seeding	Z5-2	16 d	170	0.17[a]

[a] Weight before calcination.