

Fast microwave synthesis of Pt-MFI zeolite coatings on silicon micromonoliths: application to VOC catalytic combustion

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Abstract

This paper describes the preparation of a ZSM-5 zeolite layer onto conventional Si wafers and Si micromonoliths, by using microwave-assisted seeded hydrothermal synthesis. A homogeneous ZSM-5 zeolite layer up to 680 nm was obtained over the external surface of a Si micromonolith (surface to volume ratio $>300,000 \text{ m}^{-1}$) after only 4 min of hydrothermal synthesis at 453 K. As a proof of concept, the catalytic activity of the prepared ZSM-5 coated micromonoliths, after a conventional Pt ion-exchange process, was demonstrated in the combustion of traces of n-hexane (200 ppmV) in air.

Keywords: MFI; microreactor; microwave synthesis; VOC combustion.

1. Introduction

The deployment of layers of zeolites and related functional materials can be used to enhance the performance of micro-fabricated chemical devices such as microreactors and sensors [1]. Applications of these materials, on a variety of supports, have been reported for catalysis, adsorption, membranes and optical applications, to name a few. The synthesis of well adhered stable and homogenous layers over Si based micro-structured devices was pioneered by Wan et al. [2]. Since then, different strategies, ranging from the simple deposition of zeolite particles in the microsystem, to methods involving hydrothermal synthesis, have been developed [3]. One of the

avenues explored involves the deployment of well-intergrown zeolite coatings over Si wafers, followed by micropatterning of the fabricated layers, using photolithography etching processes adapted from those employed in the semiconductor industry [4, 5]. By using these techniques, a variety of zeolite patterns can be created, with a spatial resolution of a few microns [5]. Alternatively, the underlying silicon support can be removed, creating self-standing zeolite structures. This has been used to prepare c-oriented polycrystalline silicalite cantilevers, with excellent properties as chemical sensors [6, 7].

In spite of the advances achieved, preparing a zeolite layer on silicon supports by hydrothermal processes, remains a challenge in many scenarios. The hydrothermal synthesis of zeolite layers involves an alkaline solution, often with a $\text{pH} > 13$, and temperatures typically $> 363 \text{ K}$. A relatively long time is usually required to synthesize a well-intergrown polycrystalline zeolite layer, from several hours up to several days. This means that bulk anisotropic etching of the Si substrates is likely due to prolonged exposure to synthesis conditions, and to avoid this, SiO_2 or Si_3N_4 protective layers need to be deposited on top surfaces. Other challenges in the synthesis of zeolite films on micropatterned surfaces are related to the difficulties in achieving a homogeneous growth throughout the target area. In a conventionally heated autoclave, a non homogeneous temperature profile is often developed during the initial heating period to reach the reaction temperature, and significant temperature gradients are possible during synthesis, since heat transfer mainly takes place through natural convection.

Compared to conventional heating, the volumetric nature of microwave heating presents many advantages regarding energy transfer. In particular, when microwave-assisted hydrothermal synthesis is carried out, high heating rates can be achieved, wall effects are minimized, and the development of significant temperature gradients is less likely, compared to conventional heating. Although a microwave effect, responsible for the faster synthesis, has sometimes been claimed in the literature, the acceleration effect of microwave synthesis can be explained as a result of fast and simultaneous nucleation [8, 9]. As an additional advantage, the faster synthesis attainable through microwave heating means that exposure times are reduced, and leaching of the silicon support would likely be minimized.

Although hydrothermal synthesis of Mobile Five zeolite (MFI) layers has been widely studied, the investigations on synthesis of MFI layers under microwave heating are scarcer, as shown in a recent review by Huang and Caro [9]. A main obstacle relates to the fact that, under the relatively high temperature conditions (around 453 K), the organic structure-directing agent (SDA, TPA^+), used to prepare MFI zeolite, tends to degrade under microwave irradiation [10]. Motuzas et al. [11]

synthesized MFI layers on tubular membranes under microwave heating. Their procedure was further applied to capillary tubes for which 2 h synthesis time were required to obtain a continuous film. The as-prepared membranes were tested in the pervaporation of ethanol/water mixtures, showing high water flux 1.5 kg/h m^2 and selectivity, $\alpha_{\text{EtOH/H}_2\text{O}}=54$ [12]. The mechanism of the formation of b-oriented films onto stainless-steel substrates by microwave heating has been recently studied by Li et al. [13]. The authors concluded that 20 min synthesis time was enough to grow a continuous zeolite film.

Unlike previous works, this manuscript is related to the preparation of MFI layers by microwave assisted hydrothermal synthesis on silicon substrates. Our strategy addresses the main problem of the synthesis (leaching of the Si support) by first depositing a seed of MFI crystals that reduce support exposure, and then carrying out the synthesis under microwave heating to lower synthesis times, and reducing Si anisotropic etching in the basic synthesis environment. The first part of this work studies the growth of MFI coatings over Si surfaces (silicon wafers) under microwave-assisted hydrothermal synthesis; once the synthesis conditions have been optimized, homogeneous ZSM-5 coatings are developed on the surface of macroporous Si micromonoliths. Finally, as a proof of concept, the as-prepared MFI modified microreactors were subjected to conventional Pt ion-exchange, followed by an activation process and then applied as catalytic combustors for the removal of trace concentrations of n-hexane in air. The catalytic oxidation of n-hexane, considered as a representative volatile organic compounds (VOC) molecule, has been chosen as a model reaction system of mass transfer limited reactions, since these organic pollutants are commonly present at ppm level.

2. Experimental

2.1. Synthesis of zeolite layers

Thermally oxidized <100> Si wafers purchased from Siltronic (France) were used as support for the initial study on the growth of zeolite MFI layers. The silicon oxide layer, around 700 nm in thickness, was grown on the Si wafers by a thermal oxidation process in a tubular furnace (Carbolite GHA 12/450) combining dry and humidified conditions at 1273 K during 3 h.

Once suitable synthesis conditions were established, Si micromonoliths prepared by photoassisted electrochemical etching (Figure 1) [14], identical to those already coated with silicalite type zeolite, using conventional heating [15] were also used. The so-obtained zeolite coated micromonoliths presented an extremely high external area per volume ($400,000\text{--}750,000 \text{ m}^2/\text{m}^3$) and a short diffusion path length ($<1 \mu$) and were considered as potentially highly efficient gas-solid contactors. However, they were not used in reactions, due to the difficulties in achieving a homogeneous growth of the zeolite coatings in all of the monolith channels, and also the practical difficulties involved in the integration of the zeolite coated micromonolith in a reactor structure.

In this work, we have further improved the synthesis to increase the homogeneity and reproducibility of the zeolite

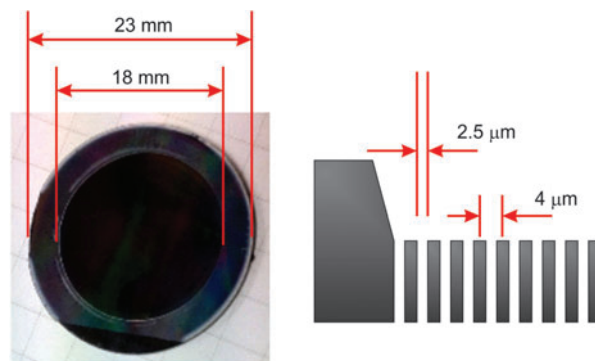


Figure 1 Si micromonolith picture and scheme showing the characteristic lengths.

coverage. To this end, the Si micromonolith samples were shaped in disks with 23 mm of total diameter, of which 18 mm correspond to the Si micromonolith. This central monolith area contains straight channels $2.5 \mu\text{m}$ wide and $220 \mu\text{m}$ long, keeping a pitch of $4 \mu\text{m}$. This yields an external surface to volume ratio above $263,000 \text{ m}^2/\text{m}^3$ for the micromonolith.

Previous to the synthesis, the Si based supports were seeded with silicalite seeds of 100 nm in size prepared by the hydrothermal route. The MFI seed synthesis was carried out in a conventional oven at 373 K during 15 h using a gel with the following molar composition: tetrapropylammonium hydroxide (TPAOH): SiO_2 : H_2O :EtOH=9:25:480:100 [16]. The reagents, TPAOH (1.0 M) as the SDA and tetraethyl orthosilicate (TEOS) 98% wt as a silicon source, were purchased from Sigma Aldrich. The seeding of the micromonoliths was accomplished by immersion of the microstructured support in a 0.4 wt% seed solution in deionized water during a few seconds. After withdrawal, the liquid was blown using hot air. By contrast, the Si wafers were seeded by spin coating of the seed solution at 4% wt in ethanol.

The synthesis gel composition for the secondary growth of MFI zeolite layer with a Si/Al=100 was $1\text{Na}_2\text{Al}_2\text{O}_4$:200 SiO_2 :14 Na_2O :9.5TPAOH:9400 H_2O . In this case, colloidal silica Ludox AS-40, sodium aluminate (Quimivita) and tetrapropylammonium bromide (Sigma Aldrich) were used as Si, Al sources and the SDA, respectively.

The microwave (MW) oven used in this study was a computer-controlled Milestone ETHOS PLUS, with a fixed frequency of 2.45 GHz. The MW Teflon lined autoclave is equipped with temperature sensors. The evolution of temperature and power supply during each experiment is automatically recorded. In all the experimentation herein described, the synthesis temperature was fixed at 453 K and the maximum power was kept at 500 W. In such a way, an SDA degradation phenomenon by MW irradiation was avoided. Under these operating conditions, the heating up to the final temperature was ensured in $<1 \text{ min}$, whatever the total synthesis time (ranging from 3 up to 30 min). After hydrothermal treatment, the samples were subjected to ultrasound during 10 min to remove any loose material inside the channels and the adhered layer remained after this treatment.

2.2. Catalytic activation of zeolite layers and reaction tests

The as-prepared zeolite coated micromonoliths were conventionally calcined in air at 753 K for 6 h, using a heating rate of 0.5 K/min. Afterwards, the ZSM-5 layer in the Na⁺ form was ion-exchange with a 2.5-mM or 5 mM solution of Pt(NH₃)₄(NO₃)₂, (Sigma-Aldrich). For such purposes, the micromonoliths were suspended in the Pt precursor solution and maintained under stirring during 24 h at room temperature. In addition, two micromonoliths without Pt and with Pt, but without zeolite coating, respectively, were prepared and catalytically tested as references. In the latter case, the bare Si micromonolith with the 700 nm SiO₂ layer, was impregnated by a classical incipient wetness procedure, with a 2.5-mM solution of Pt (NH₃)₄(NO₃)₂ to obtain Pt loadings similar to those in zeolite coated monoliths.

After assembly and proper sealing in the reaction chamber, the micromonoliths were studied in the catalytic combustion of 200 ppmV n-hexane in air. The feed consists of 30 Nml/min, with an equivalent carbon content of 590 mgC/m³. Such experiments were performed in an experimental set-up previously described [17]. Before carrying out the catalytic activity tests, the Pt exchanged ZSM-5 micromonoliths were calcined in air up to 623 K for 3 h using a heating rate of 0.2 K/min.

3. Results

All the samples prepared in this work are listed in Table 1. The initial set of experiments was carried out to optimize the hydrothermal synthesis onto SiO₂+Si wafers. The synthesis time was varied from 3 to 30 min. Figure 2 shows the top view and the cross section of the zeolite layers synthesized with the reaction time. In all cases, “c oriented” MFI layers, with the typical columnar morphology [11, 12] exhibiting a good intergrowth were observed. In the seeded hydrothermal synthesis, zeolite crystals are expected to grow from the seed layer and therefore a more diluted synthesis gel is employed, which is expected to avoid homogeneous nucleation in the bulk of the liquid. In spite of this, Figure 2 shows the presence of some non-integrated material, which likely corresponds to crystals nucleated and grown in the bulk of the solution and

then precipitated on the zeolite film. However, on the whole, the SEM micrographs of Figure 2 show a homogeneous, well-intergrown film on top of the Si support.

The required crystallization period of zeolites under microwave heating depends on many variables, including the type of MW, the nature of the substrate, the size of the reactor and the distribution of the MW energy. On this basis, it is possible to understand the differences reported in the literature [18]. Synthesis times as short as 1 min or 5 min were reported for ZSM-5 [7]. In our previous work [11], we reported that a synthesis time of 2 h at 433 K was necessary to obtain a high quality MFI membrane, 1.2 μ thick, in ceramic capillary tubes of 50 mm length, placed vertically in the autoclave. However, in this case a catalytic layer (instead of a permselective membrane) is the objective, and therefore lower synthesis times can be employed.

The evolution of thickness layer with synthesis time is depicted in Figure 3. As the Si substrates have been previously seeded, MW heating mainly increases the zeolite crystals growing rate, although some additional nucleation cannot be excluded, as discussed above. The high energy input causes a quick heating up of the reacting mixture. Consequently, a rapid initial growth in the thickness of the zeolite layer could be observed, which decreases somewhat as the nutrients are depleted. Therefore, MW heating is especially fruitful for secondary growth of membranes, where a seeded surface is brought into contact with a secondary growth synthesis gel, to grow a continuous layer at low supersaturation.

Figure 4 shows the Si micromonolith after seeding by immersion as described above. It can be observed that the seed layer covers homogeneously the support, which provides a homogeneous surface to promote the secondary growth of the zeolite film and is also useful in reducing the etching rates on the Si support. The seeded micromonoliths were then subjected to hydrothermal synthesis. The samples, after 3 min of MW assisted hydrothermal synthesis, are depicted in Figure 5. Although the coverage by MFI seeds and the short synthesis time used (i.e., 3 min), helps to prevent Si dissolution, some etching is unavoidable, especially if bald spots in the seed layer exist. Some examples of typical anisotropic etching of <100> Si plane could be easily identified as the pyramidal hollow spaces under the zeolite layer in Figure 5C. Nevertheless, the

Table 1 Samples prepared in this work.

Sample	Support	ZSM-5 synthesis conditions			Pt activation	
		Seeding	Temp/Wmax	Time	Method	Precursor concentration
SiW3	Si wafer	Spin-coating	453 K/500 W	3 min	–	–
SiW6	Si wafer	Spin-coating	453 K/500 W	6 min	–	–
SiW10	Si wafer	Spin-coating	453 K/500 W	10 min	–	–
SiW30	Si wafer	Spin-coating	453 K/500 W	30 min	–	–
SiμM-1	Si μmonolith	–	–	–	–	–
SiμM-2	Si μmonolith	–	–	–	Incipient wetness	2.5 mM
SiμM-3	Si μmonolith	Immersion	453 K/500 W	3 min	Ion exchange	5 mM
SiμM-4	Si μmonolith	Immersion	453 K/500 W	3 min	Ion exchange	2.5 mM

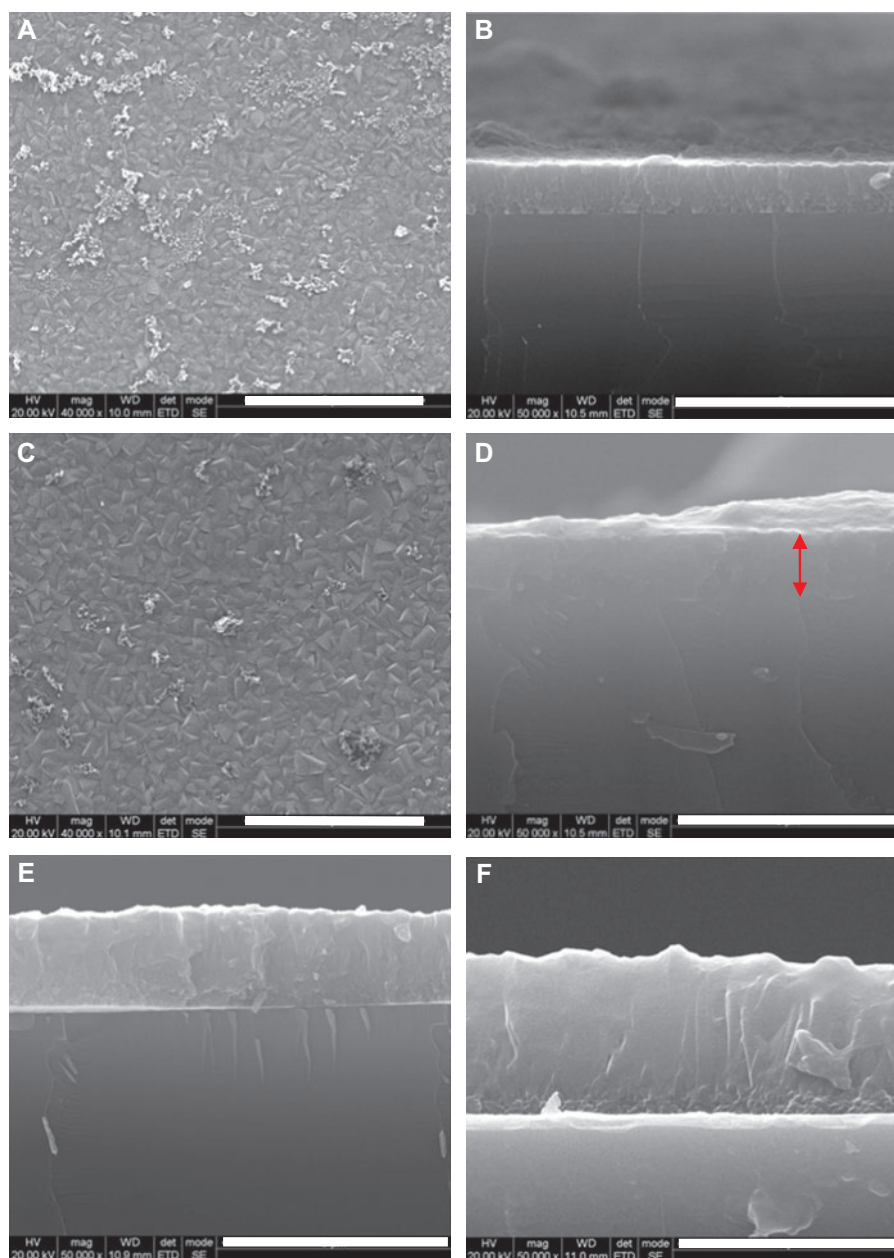


Figure 2 SEM images, ruler corresponds to 3 microns, of zeolite coatings on a thermally oxidized silicon wafer after hydrothermal microwave synthesis at different times: (A), (B) 3 min top view and cross section, (C), (D) 6 min top view and cross section, (E) 10 min cross section and (F) 30 min cross section.

extension of these defects seems to be limited, as top views of the micromonolith surfaces after hydrothermal synthesis show a complete coverage with a well intergrown layer. Figure 5A also shows that coating of the microchannels is uneven, and will need further development. Thus, some of the pore openings are partly blocked by zeolitic material, which hinders access to the catalyst and may give rise to an uneven flow distribution across the monolith. However, the blocking seems to take place mainly at the channel mouth, while the inside of the channels seems to have a homogeneous coverage (Figure 5B). From the cross section, SEM images (Figure 5C) show that the ZSM-5 layer thickness can be estimated at around 350 nm, giving an estimation of the ZSM-5 loading around 16.5

mg for the Si micromonolith. The channel mouth accumulation of zeolite material which is observed in Figure 5A, can be explained as a consequence of the mass transfer resistance during hydrothermal synthesis. Initially, the seeded channels are filled with the synthesis gel, but this is rapidly depleted by the reaction, and zeolite precursors have to be replenished from the surrounding solution. Because of the narrow size of the monolith channels ($2.5\ \mu\text{m}$), access of the synthesis gel to the growing layer inside the channels is limited, and growth takes place mainly at the channel mouth, as seen in Figure 5A. This problem could be alleviated by using forced flow of the precursor solution into the monolith channels and will be investigated in future works.

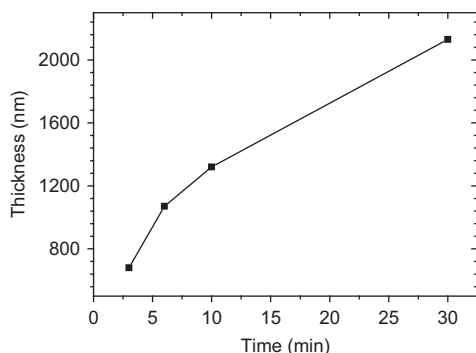


Figure 3 Thickness of zeolite layer vs. synthesis time in zeolite coatings on silicon wafer with a silicon oxide layer. Synthesis temperature=453 K. Maximum microwave power=500 W.

In spite of these problems, the as-prepared ZSM-5 coated micromonolith provides a large external surface to volume ratio for catalytic applications, with short diffusion lengths both in the channel and in the catalyst layer. After introducing Pt by the exchange procedure already explained, the Pt/ZSM-5 coated micromonoliths were used in the combustion of n-hexane at low (200 ppm) concentration levels. Two different Pt loadings (prepared by exchange with 2.5 mM and 5 mM Pt solutions, respectively), were used, and the reactor performance was also compared with that of a micromonolith, without the zeolite layer directly impregnated with Pt and also with that of a bare Si micromonolith. The contact time for all the catalytic tests was kept constant at 34 ms. It is worthwhile to underline that this value corresponds to gas hourly space velocity values considerably higher (above 100,000 h⁻¹) than those commonly used for conventional monolith testing 3500–10,000 h⁻¹ [19, 20]. The reaction results are shown in Figure 6. As expected, as the metal concentration increases in the Pt exchange solution for the zeolite coated micromonoliths, the light-off curves shift towards lower temperatures. The most active micromonolith is the 5 mM Pt exchanged ZSM-5, in which the temperatures required for 50%, (T_{50} or light-off temperature) and 90% (T_{90}) conversion were 488 K and 541 K, respectively. For the 2.5 mM Pt exchanged ZSM-5 the T_{50} and T_{90} values were 35 K and 56 K higher, respectively.

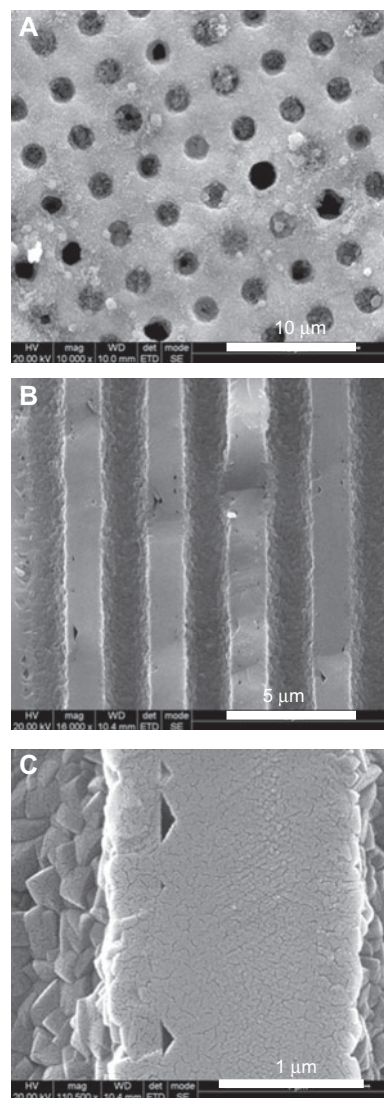


Figure 5 SEM images of microwave synthesis of ZSM-5 on silicon micromonoliths.

The bare micromonolith showed a low activity, with 18% conversion at 573 K, whereas the Pt impregnated Si micromonolith needed 565 K to attain 50% conversion. The

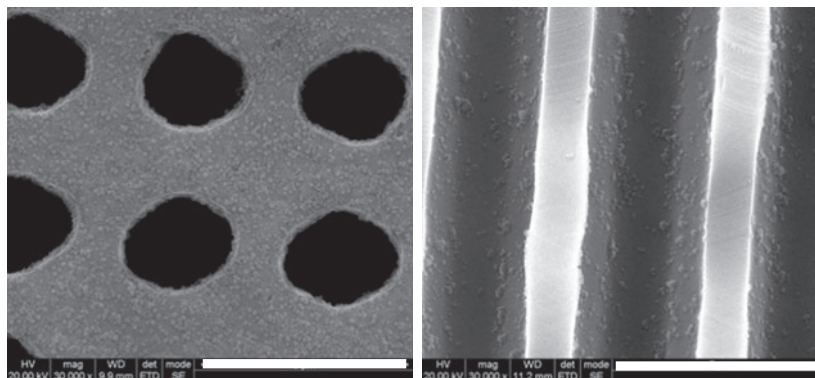


Figure 4 SEM images, ruler corresponds to 5 microns, of Si micromonoliths after coating with MFI seeds, top view and cross section.

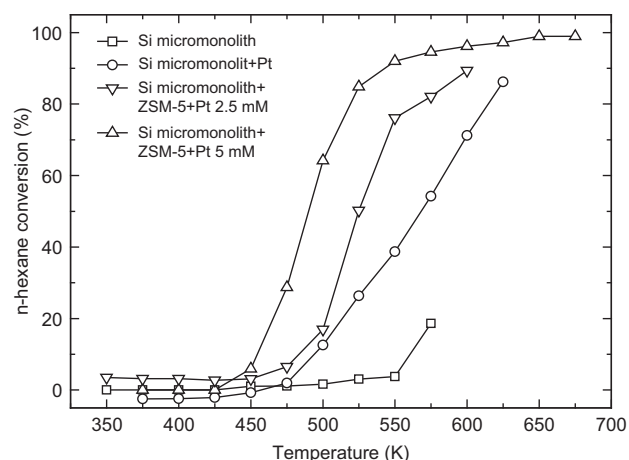


Figure 6 Hexane conversion vs. temperature. Catalytic combustion of 200 ppm n-hexane in air. $Q=30$ Nml/min.

results obtained with the zeolite-coated micromonoliths are comparable to previous results in our laboratory [16], using a conventional stainless steel microreactor (500 μ channel diameter), with $T_{50}=464$ K and $T_{90}=494$ K, albeit at a higher contact time of 41 ms. There are also related works in the field of VOC removal with metallic monolith type structured reactors, using metal oxides as the catalytic phase. As an example, light-off temperature values of 503 K were found for 300 ppmV of toluene over MnCu oxide [18] and 583 K for 1200 ppmV over MnOx/Al₂O₃ [19] washcoatings operating at 10,000 h⁻¹.

4. Conclusions

In summary, it is possible to synthesize a thin (350 nm) zeolite layer by MW-assisted seeded hydrothermal synthesis in <4 min. This short synthesis time, and the zeolite seed layer, largely prevent chemical etching of the silicon substrate, making it possible to prepare zeolite layers on silicon microfabricated monoliths. The synthesis method requires optimization to avoid partial blocking of channels by zeolite deposits at the channel mouth, which hinders reactant access to the catalyst and probably gives rise to an uneven flow distribution in the monolith. In spite of this, the Pt-exchanged monoliths show remarkable catalytic activity, with combustion temperatures comparable to those previously reported for stainless steel microreactors with full catalyst access.

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