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Monolithic catalysts as more efficient three-phase reactors

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Abstract

Monolithic reactors are an attractive alternative to conventional multi-phase reactors. Advantages are the low pressure drop, the absence of a need for a catalyst separation, and the large geometrical surface area. The main disadvantage is, however, the lack of practical experience with monolithic reactors. A pilot-scale study has been carried out to evaluate the performance of a monolithic reactor on a larger scale. The results of this study have demonstrated that a higher productivity can be obtained for a monolithic reactor compared to a trickle-bed reactor for a solid catalysed gas–liquid reaction that is mass transfer limited in the gas-phase reactant. A higher selectivity has been demonstrated for the selective hydrogenation of benzaldehyde towards benzylalcohol when a monolithic reactor is used instead of a trickle-bed reactor as a result of the narrower residence-time distribution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Monolith; Hydrogenation; α-Methylstyrene; Benzaldehyde; Mass transfer; Trickle-bed

1. Introduction

Although monolithic catalyst supports are widely used in exhaust gas cleaning, their application in other types of catalytic processes is limited [3]. One of the exceptions is the hydrogen peroxide production using the anthraquinone process. Monolithic catalysts can be used as an attractive alternative in three-phase operation to both slurry and trickle-bed reactors. Advantages of monoliths are the absence of a need for filtering, low pressure drop, high geometrical surface area, safer operation, easy scale-up, and the absence of maldistribution problems (provided the liquid is properly distributed at the inlet). The major disadvantage of monolithic catalyst systems is the lack of experience in larger scale processes.

To demonstrate the feasibility of using monoliths in larger scale three-phase reaction systems, a pilot-scale set up for hydrogenation reactions has been built. In this study a comparison between a monolith and trickle-bed reactor will be presented.

In a monolithic channel a special type of flow occurs: Taylor or bubble-train flow (Fig. 1). In this type of flow, gas bubbles and liquid slugs move with constant velocity through the monolith channels, the gas is separated from the catalyst only by a very thin liquid film. For this flow regime, a higher mass transfer of gas to the catalyst is expected compared to that of a trickle-bed. The better plug-flow behaviour in the reactor for this flow regime (gas and liquid have a very sharp residence-time distribution) is expected to result in higher selectivity towards the desired product in selective reactions with unwanted consecutive reactions.

A comparison between monolithic and trickle-bed reactors at their optimal operating conditions is presented for model reactions showing the potential for rate and selectivity enhancements of a monolithic reactor.

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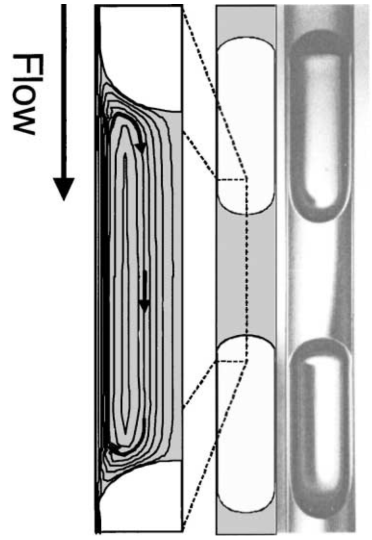

Fig. 1. Taylor-flow in capillary. The CFD picture (left) shows the liquid circulation patterns.

Two hydrogenation reactions were studied (Fig. 2). The hydrogenation of α-methylstyrene was carried out to determine the performance of both reactor types for a (hydrogen) mass transfer limited reaction. The selective hydrogenation of benzaldehyde to benzylalcohol was carried out to examine possible differences in selectivity of both types of reactors.

2. Experimental

2.1. Catalyst preparation

2.1.1. Washcoating of monoliths

Bare cordierite monoliths are not optimally suited for the preparation of catalysts, since the surface area is low (typically 0.7 m^2/g) and the metal-support area is also much less than for alumina. Therefore, the monolithic supports were washcoated with a layer of γ-alumina using a sol–gel method. A sol was prepared by mixing 0.3 M nitric acid with pseudo-boehmite (AlOOH, Pural SB1 from Condea Chemie) and urea in the weight ratio of 5:2:1. The sol was mixed for approximately 5 min using a high shear mixer. The dried monoliths were then dipped (submerged) in the sol for 30 min. The quality of the sol was checked by measuring the viscosity before and after dipping. The viscosity of a proper sol was about 20 mPa s at the start and the end of dipping.

Excess sol was removed by emptying the monolith channels by pressurised air. The monoliths were dried overnight at room temperature under continuous rotation. The monoliths were then dried at 363 K for at least 1 h and then calcined for 2 h at 673 K (heating and cooling rate: 10 K/min). In this manner a 9 wt.% loading of γ-alumina was obtained, having a surface area of approximately 240 $m^2/g_{alumina}$. Monoliths with cell densities of 200, 400, and 600 cpsi (cells per square inch) were used with a 1 cm diameter and 25 cm length.

2.1.2. Metal deposition

Egg-shell type nickel catalysts were prepared by deposition precipitation [2]. A solution of 0.1 M $Ni(NO_3)_2$ and 1.0 M urea was prepared. The dried washcoated monoliths were kept stationary in this solution. The dried γ-alumina (Akzo Ketjen 000-1.5E) extrudates (1.7 mm diameter, 5 mm long) were stirred mildly (to prevent attrition) in the solution. The solution was heated to 353 K for 24 h to have the urea decompose slowly into ammonia and carbon dioxide, resulting in a slow decomposition of nickel hydroxide

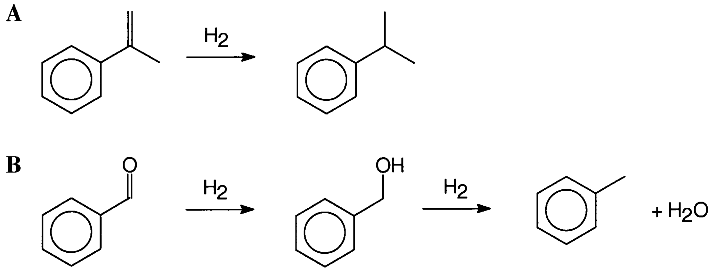

Fig. 2. Model reactions for the comparative study between monolith and trickle-bed reactor. (A) Hydrogenation of α-methylstyrene. (B) Hydrogenation of benzaldehyde to benzylalcohol with (unwanted) consecutive reaction to toluene.

on the catalyst. The monoliths were then dried at room temperature in air while continuously being rotated. The extrudates were dried in air at 353 K. The catalysts were then calcined at 673 K for 2 h (heating and cooling rate: 10 K/min). The catalysts were reduced in 50% hydrogen in argon at 823 K for 3 h (heating and cooling rate: 5 K/min). After cooling to room temperature (in hydrogen) the catalysts were passivated to prevent nickel aluminate formation or sintering of the catalyst by rapid oxidation of the nickel particles on exposure to air. This was done in a stream of nitrogen, in which over a period of 2 h, the oxygen content was slowly increased from 0 to 20%. A nickel loading of 7 wt.% on the extrudates was prepared and a nickel loading of 1 wt.% on the monoliths was prepared. The nickel loading on the monoliths was deliberately kept lower, since the amount of alumina available was also lower.

2.1.3. Catalyst analysis

Scanning electron micrographs (SEMs) and transmission electron micrographs (TEMs) were made to evaluate the deposition of the washcoat and the nickel. The nickel loading of the catalysts was determined using X-ray fluorescence (XRF). The spent catalysts were checked for carbon deposits using thermogravimetric analysis/differential scanning calorimetry (TGA/DSC).

2.1.4. Catalyst testing

In a monolithic-pilot reactor the performance of a monolithic catalyst has been compared to that of a trickle-bed reactor. In this set up, both the monolithic catalysts, 2 m in length and 1 cm diameter; and 47 mm in diameter and 25 cm length trickle-bed, have been tested. The system was operated as a mixed batch system containing 10–15 l of liquid, with the liquid being pumped through the externally placed reactor. The gas was not recycled. Gas and liquid were fed in co-current downflow through the reactor. The liquid was distributed by means of a showerhead. With the monolithic catalysts the showerhead produced a froth on top of the monolith, ensuring an even gas/liquid distribution. For the trickle-bed a 10 cm layer of alumina extrudates without nickel was used to obtain an even distribution over the catalyst bed. Samples were taken from the liquid entering and leaving the reactor. Analyses of the liquid were performed using a gas chromatograph.

In Table 1 it can be especially seen that the superficial velocities in the monolithic and trickle-bed reactor differ significantly. This difference is because for both reactors, gas and liquid flows were set to the typical conditions for these reactors to operate in a hydrodynamically stable regime. In a monolithic reactor, low superficial velocities (<0.1 m/s) will easily cause maldistribution, whereas the higher velocity used an even distribution which is easily obtained. The trickle-bed reactor on the other hand was operated at much lower velocities, since otherwise the trickle-flow regime could not be obtained. Varying the gas and liquid velocity in the trickle-bed reactor did not significantly change the productivity of the reactor, indicating that maldistribution or partial wetting was not an issue. The even distribution of the liquid over the bed for the distributor used were confirmed by cold-flow experiments in a glass reactor using

Table 1
Experimental conditions for α-methylstyrene and benzaldehyde hydrogenation in a monolithic and trickle-bed reactor

	Monolith	Trickle-bed
Length (m)	2	0.25
Diameter (mm)	10	47
Support	Cordierite with ∼9 wt.% γ-alumina washcoat	γ-Alumina extrudates, 5 mm long, 1.7 mm diameter
Catalyst	∼1 wt.% Ni (egg-shell)	7 wt.% Ni (egg-shell)
Reactor porosity (–)	0.75	0.4
Superficial velocity (m/s, liquid and gas)	0.2	0.01
	α-Methylstyrene hydrogenation	Benzaldehyde hydrogenation
Temperature (K)	373	423
Pressure (bar)	10	15

colour tracer. The reactor diameters were chosen to have equal gas and liquid flow rates in both reactors.

Monolithic catalysts were also tested on a smaller scale using a turbine-stirred autoclave. In this autoclave reactor 5 cm long, 1 cm diameter monolithic segments were tested while gas and liquid were being rapidly recirculated.

To determine to what extent differences in activity between monolithic and extrudate catalysts will result of the structure, the activity of the milled catalysts were determined in a slurry autoclave reactor.

3. Results and discussion

3.1. Mass transfer

An example of a measurement for an α-methylstyrene hydrogenation is given in Fig. 3. Initially, the concentrations are on a straight line, confirming a zero reaction order in the α-methylstyrene concentration, as should be the case for a mass transfer limited reaction in hydrogen. Only when higher total conversions were reached, the reaction rate drops, since then the mass transfer of the liquid reactant (α-methylstyrene) and the kinetics start to control the reaction rate. The activities that can be determined from the mass transfer experiments are given in Table 2. It can be seen that a monolithic reactor has a 50% higher productivity per reactor volume than a trickle-bed reactor, even though the porosity of the monolithic reactor is relatively high.

The higher productivity of the monolith can be explained by the thin liquid film that separates the gas bubbles from the monolith wall in the Taylor-flow regime. To rule out the rate enhancements that could be caused by differences in the activity of the catalyst itself, the intrinsic performance of the milled catalysts was compared in a slurry system. These experiments showed that under these conditions the trickle-bed catalyst had even higher activity (3.6×10^{-5} versus 1.5×10^{-5} mol/$g_{catalyst}$/s), clearly demonstrating that the better performance of the monolithic catalyst is the result of the structure. The higher intrinsic activity of the trickle-bed catalyst can be explained by the higher nickel loading. The extremely low pressure drop of a monolithic reactor allows for the use of higher cell densities (up to 1100 cpsi is available) for which the productivity will be even higher.

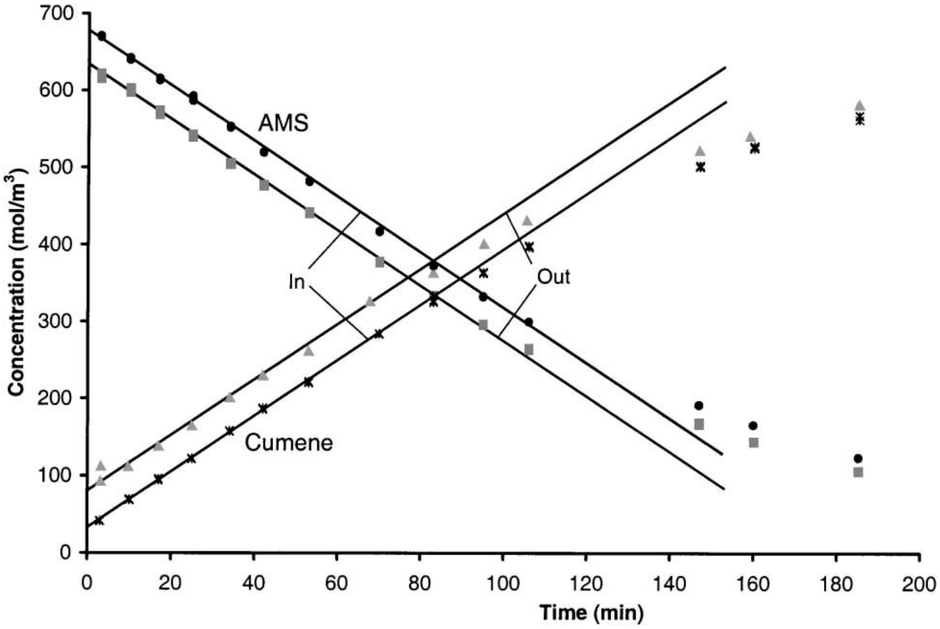

Fig. 3. α-Methylstyrene (AMS) and cumene concentrations with time at the reactor entrance and exit for a typical α-methylstyrene hydrogenation experiment over a monolithic catalyst (400 cpsi).

Table 2
Activities for both a monolithic and trickle-bed reactor for the mass transfer limited hydrogenation of α-methylstyrene over an egg-shell nickel catalyst (373 K, 10 bar H_2)

Activity per	Units	Monolith (400 cpsi)	Trickle-bed
Reactor volume	$mol/m^3_{reactor}/s$	6.2	4.6
Geometrical surface area	$mol/m^2_{geom}/s$	1.9×10^{-3}	2.0×10^{-3}
Catalyst amount	$mol/g_{catalyst}/s$	1.1×10^{-5}	6.2×10^{-5}
Nickel amount	$mol/g_{nickel}/s$	9.8×10^{-4}	8.4×10^{-5}

From the measured activities it is possible to calculate the gas-catalyst mass transfer parameters, assuming that the liquid is saturated with gas at the gas–liquid interface. For the monolithic system (400 cpsi), $k_{gs} \times a$ is $0.13\,s^{-1}$, while for the trickle-bed this value is $0.09\,s^{-1}$. From the study by Mazzarino and Baldi [4] for a mass transfer limited α-methylstyrene hydrogenation over a trickle-bed reactor with similar superficial velocities and geometrical surface area also, the $k_{gs} \times a$ value can be calculated. Their reported value ($0.04\,s^{-1}$) is considerably lower than our values, indicating that the measurements carried out in our study indeed were mass transfer limited. For monolithic catalysts no appropriate gas-catalyst mass transfer parameters were available. It is, however, possible to estimate these parameters using the mass transfer through the Taylor-flow film model, as reported by Andersson et al. [1]. In their model a film thickness was calculated separating the gas from the catalyst wall, with the mass transfer of the gas assuming to occur via diffusion. The model yields a $k \times a$ value for the monolith reactor of $0.73\,s^{-1}$. Partly, this difference can be explained by two effects. Firstly, in practice the liquid film in a square channel will not have a uniform thickness. As a result of the surface tension of the liquid, the gas bubbles will have a rounder shape, with the liquid film in the corners being thicker. It can be calculated that in the corners the film will be 160 μm thick, compared to 20 μm in the middle. This effect is schematically depicted in Fig. 4A. Secondly, the model calculates a film thickness over a smooth surface. In practice, the surface is rough. From SEM micrographs it was determined that the surface has pits and bumps of 5–10 μm, resulting in a thicker average liquid film, and as a result a slower mass transfer. This aspect is schematically depicted in Fig. 4B. These two effects combined were able to explain the lower mass transfer rate measured and if these effects are included the model and measurement are in fair agreement. Finally, the catalyst surface will not be completely covered with nickel. As a result not the complete surface is active, resulting in a lower than ideally possible activity for pure external mass transfer limitations.

The importance of the Taylor-flow for the gas-catalyst mass transfer was checked by carrying out a full-liquid experiment. In this experiment, only liquid saturated with hydrogen was fed to the reactor. This experiment yielded an activity for the same 400 cpsi monolithic catalyst of only $1.5\,mol/m^3/s$. This activity is corrected to the activity which would be obtained if

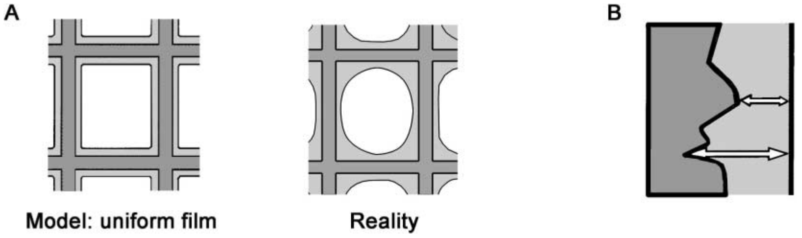

Fig. 4. Schematic representation for slower mass transfer in measurements compared to model predictions. (A) Thicker film in monolith channel corners due to surface tension. (B) Thicker film due to uneven surface.

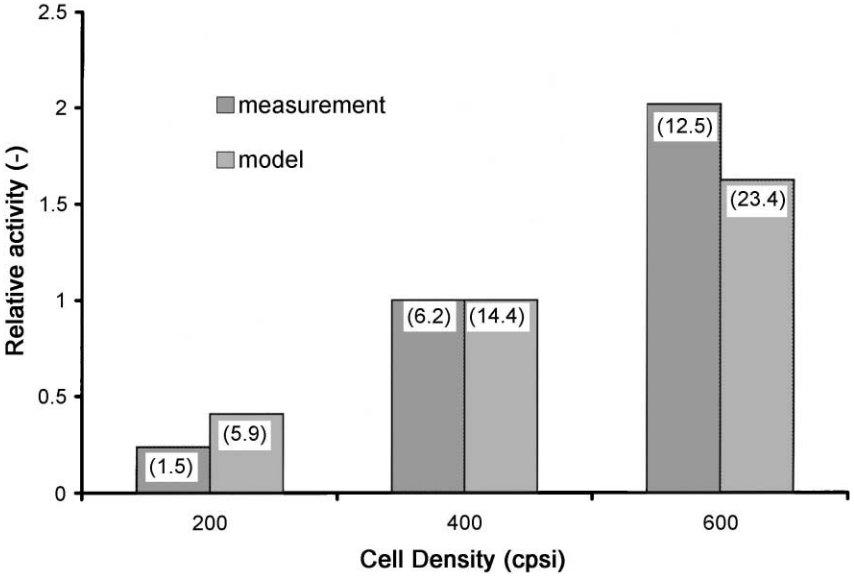

Fig. 5. Measured and modelled relative activities for AMS hydrogenation over Ni-monolithic catalyst as a function of cell density (values in brackets were actual activity values (mol/m^3/s)).

the liquid would remain saturated with hydrogen over the entire reactor length (i.e. multiplied by a factor to account for the hydrogen depletion over the reactor length). This experiment clearly indicates that the mass transfer of hydrogen via the bulk liquid is much slower than the transfer through the thin liquid film.

In Fig. 5, the activity for monolithic catalysts is given for the different cell densities used, together with predicted rates based on the mass transfer models currently available. It can be seen again that not only the absolute values for all activities are higher, but also the cell density dependence of the model is weaker than the observed dependency. This indicates the simple film-diffusion model is insufficient for predicting the gas-catalyst mass transfer in a monolith.

3.2. Selectivity enhancement

The selective hydrogenation of benzaldehyde for a monolithic catalyst showed a high selectivity to benzylalcohol, while a trickle-bed catalyst had a much lower selectivity. Exemplary pilot experiments are shown in Fig. 6. The higher selectivity of the monolithic reactor can be explained by the sharper residence-time distribution in the monolithic reactor. If in part of the reactor the liquid resides longer, loss of selectivity occurs. The straight channels in a monolith rule out this possibility, while in a trickle-bed reactor stagnant zones can be present due to an inhomogeneous bed. A second cause for the difference in selectivity of the two systems might be a difference in the thickness of the catalytic layer. The benzaldehyde hydrogenation is not externally mass transfer limited in hydrogen (the pilot experiments showed an activity of typically $0.8\,\mathrm{mol/m^3_{reactor}/s}$ for a 400 cpsi monolith and $2.2\,\mathrm{mol/m^3_{reactor}/s}$ for a 600 cpsi monolith). As a result, the reaction will not only take place at the external surface of the catalyst, but also further inside the catalyst. The wall thickness of the monolithic catalysts is only 0.1–0.2 mm, while the extrudates of the trickle-bed catalyst were 1.7 mm diameter. Since benzylalcohol produced further into the centre of the support has a longer diffusion distance to the liquid bulk, this will sooner be converted to toluene. The fact that the benzaldehyde hydrogenation reaction is not purely mass transfer controlled does account for the relatively higher activity of the trickle-bed system in Fig. 5 compared to the 400 cpsi monolith (with a comparable external surface area). Since the porosity of a trickle-bed is much lower than the porosity of the

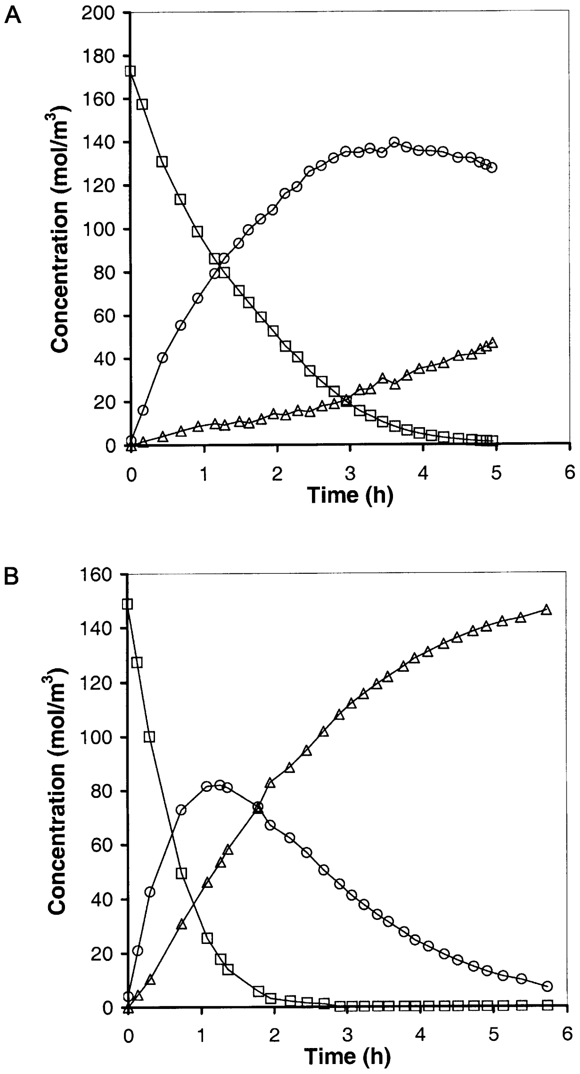

Fig. 6. Benzaldehyde hydrogenation over: (A) monolithic (400 cpsi) and (B) trickle-bed reactor (200 g benzaldehyde in 10 l toluene, 15 bar H_2, 410 K, concentrations with time at reactor inlet: (□), benzaldehyde; (○), benzylalcohol; (△), toluene produced).

monolith (0.4 versus 0.75), the trickle-bed contains more catalyst and thus has a higher production rate.

Fig. 7 summarises the selectivities obtained at 50% conversion for different experiments with different reactor systems. The highest selectivities are obtained for the reaction systems with a small diffusion distance (slurry and monoliths) and the absence of a residence-time distribution (batch experiments). The pilot-scale monolith experiments exhibit a slightly lower selectivity in which the selectivity is higher for 600 cpsi monoliths than for 400 cpsi monoliths. This can be explained by the small diameter of the monolith reactor used. The channels at the edge of the monolith have to be smaller than the channels in the middle to obtain the round shape, as a result the liquid will reside longer in these channels and sooner react to toluene. The 600 cpsi monoliths have smaller channels than the 400 cpsi monoliths, and therefore, the relative amount of deformed channels is smaller (19 versus 24%) and the selectivity is higher for the 600 cpsi monolith. A second explanation for the difference in selectivity is the difference in wall thickness between 400 and 600 cpsi monoliths (0.16 versus 0.11 mm). The 600 cpsi monoliths has therefore a shorter diffusional path and can obtain better selectivities. The experiments in the rapid circulation autoclave reactor did not show a cpsi dependence, since for these experiments the short (5 cm) monolith length did not have a significant residence-time distribution over the monolith.

To evaluate the practical applicability of the nickel monolithic system for the benzaldehyde hydrogenation, a pilot run was also carried out using a pure benzaldehyde feed, since diluted systems are industrially unwanted. Undiluted, almost no toluene was produced which can be explained by the kinetics of this reaction system (Langmuir–Hinshelwood kinetics with a strong adsorption of benzaldehyde on the catalyst [5]). The only significant side product observed in the diluted systems was toluene. In the undiluted run, this product, however, was virtually not produced up to the moment all benzaldehyde had been converted (Fig. 8). As a side product, a heavy component was found, which was not formed in the diluted experiments. GC–MS analysis showed the product is most likely a hydrobenzoin-alike product from a reaction between benzylalcohol and benzaldehyde. After a total run-time of 80 h this catalyst showed a deactivation of about 25%. TGA–DSC analysis showed a small amount (0.5 wt.%) of carbonaceous that deposit was present on the catalyst, most likely being the cause of this deactivation. A better catalyst (i.e. no deactivation and no heavy side product) can probably be produced if silica is chosen as a support for both carbon formation on the catalyst and production of the heavy component most likely occur over the

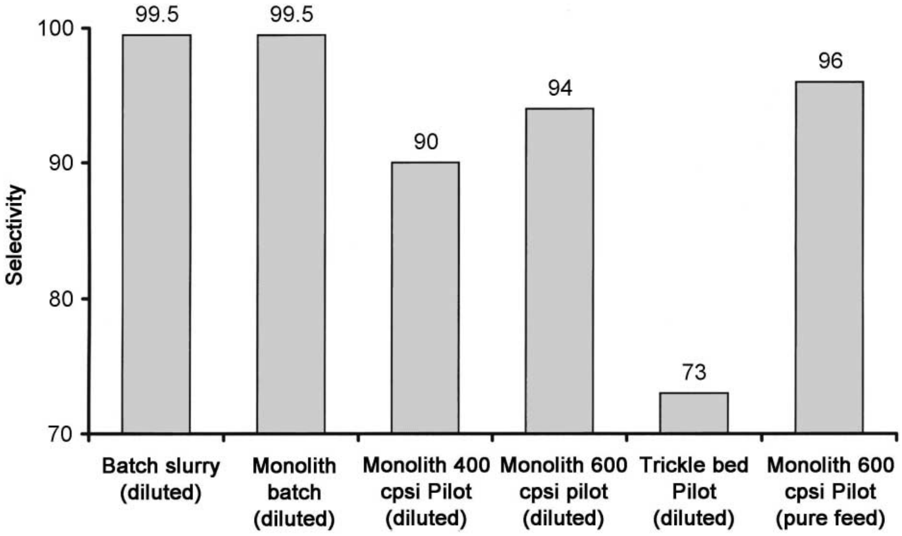

Fig. 7. Selectivities at 50% conversion for hydrogenation of benzaldehyde in different reactor systems.

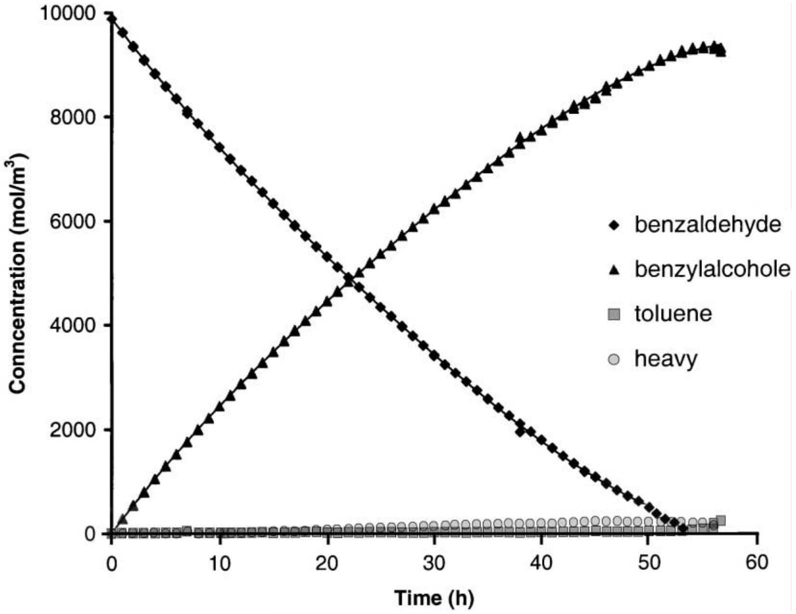

Fig. 8. Concentrations as a function of time for a pilot-scale run with undiluted benzaldehyde (15 bar H_2, 410 K, 600 cpsi alumina washcoated nickel monolith).

slightly acidic sites present on the alumina. Nevertheless, even the currently available (alumina supported) catalyst demonstrate a strong potential for application in a benzaldehyde hydrogenation process.

4. Conclusions

Monolithic catalysts were promising systems to replace catalysts in conventional multiphase reactors. Not only do monoliths have operational advantages (catalyst separation, pressure-drop, etc.) but the performance of a monolith has also been demonstrated to be better. Pilot-scale experiments to compare a monolith and a trickle-bed catalyst system have demonstrated higher productivity in a monolithic reactor for a mass transfer limited reaction and higher selectivities for the selective hydrogenation of benzaldehyde.

Acknowledgements

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