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Hurdles and solutions for reactions between gas and liquid in a monolithic reactor

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Abstract

In this paper, proof of principle experiments and exploratory work that solves the problem of ensuring that a gaseous and a liquid reactant are available at the catalytically active site at the same time by separating the reaction and the transport of the gaseous reactant. The equipment consisted of an autoclave in which a feed was saturated with hydrogen, a reactor with a catalyst coated on a monolith, a pump to circulate the feed/product stream, and devices to control and monitor the process.

A lot of information of how the process can be practised was gathered during the work. Conversion per pass should be below the amount of hydrogen that can be dissolved in the liquid to avoid coke deposition (and hence deactivation) of the catalyst. The effectiveness of the catalyst coated on the monolith was found to be 100%.

Several variations of the process design and catalysts used were explored. Integration of the monolith with a heat exchanger will obviously allow for the use of the process for very exothermic reactions like (nitro)benzene hydrogenation. A monolith to which Rh-cyclooctadiene-1,2-bis-diphenylfosfino-ethane (a homogeneous catalyst) was tethered was equally active in hydrogenation of 1-hexene as Rh-cyclooctadiene-1,2-bis-diphenylfosfino-ethane tethered to a standard alumina. This allows (fine)chemical producers to repeatedly use the expensive homogeneous catalysts without the need for separation of the catalyst from the reaction mixture.

Keywords: Monolithic reactor; Hydrogenation; Gas-liquid mixing; Homogeneous catalyst; Tethering

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1. Introduction

The advantages of a structured reactor coated with a layer of catalytically active material have been widely publicized and recognized. Among these are:

- Low pressure drop.
- Short diffusion path to/from the active site for reactants and products, which decreases the chance of side/consecutive reactions and hence increases selectivity.
- High "external" surface area, i.e. a high interfacial area between the catalytically active material and the phase with the reactant(s). This allows for high mass transfer rates and hence higher process intensity.

Despite the advantages outlined above, few structured reactors are used in the chemical industry. Presently, only the reduction step of anthraquinone in the manufacturing of hydrogen peroxide [1] and a clean-up step for the selective oxidation of *ortho*-xylene to phthalic anhydride [2] are practised using a structured reactor. This is due to two reasons:

1. The structured reactor contains less catalyst than a fixed bed and hence requires a more stable catalyst than a fixed bed or batch process.
2. Many chemical processes are three-phase processes, in which one of the reactants resides in

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> the gas phase and the other in the liquid phase. In order to obtain good productivity and selectivity, extremely good mixing of the gas phase with the liquid phase is required. This is the justification for all the work devoted to understanding the hydrodynamics of structured reactors and Taylor flow.

An alternative to the mixing of the gas phase and the liquid phase inside the reactor is rotating the monolith around a horizontal shaft [3], which results in alternate contact of the monolith with the liquid phase in the bottom of the reactor and the gas phase in the top of the reactor.

Another alternative to the mixing of the gas phase and the liquid phase inside the reactor is saturating the liquid with gas, followed by passing the saturated liquid through the structured reactor. This paper describes the laboratory setup that demonstrates this process design and discusses a number of results obtained with the setup. Hydrogenation of tetralin was carried out using monoliths loaded with precious or base metal. In further work, we used an immobilized homogeneous catalyst to hydrogenate 1-hexene. This opened up a whole arena of fine chemical applications that currently are suffering from separation problems.

2. Experimental

A test unit was constructed according to Fig. 1. The liquid in this schematic drawing is circulating anti-clockwise. The left-hand part of the unit is used to saturate the liquid with hydrogen, the catalyzed reaction takes place in the right-hand part of the unit. Important elements in the design are an autoclave in which the liquid is saturated with hydrogen, the reactor, a back-pressure regulator and the pump. The back-pressure regulator is needed to provide the pump with the necessary resistance to work properly. In the absence of gas, pressure fluctuations can easily become very large. We, therefore, added an expansion vessel. The process was followed with a LIQUIFLOW® device to measure the flux of circulation liquid and the in-line UV-cell to measure aromatic conversion.

The monolith had an outer diameter of 2 cm and was 15 cm long. It was mounted on a specially designed reactor pipe. To prevent bypassing of the monolith, it was “locked” in between two Kalrez® seals (see Fig. 2). The effective monolith volume (area) was thereby reduced to 58%. The liquid was flowing up through the monolith assuring good wetting. The inlet temperature was measured with a thermocouple placed just upflow the monolith. In a latter stage, also the temperature profile was checked *inside* one of the channels of the monolith.

Several measures were taken to ensure that the reactions are indeed carried out with dissolved gas. The first was to saturate the liquid at a ~5 bar lower pressure (30 bar working pressure, 25 bar saturation pressure) than carrying out the reaction. The second was to use hydrogen as the gaseous reactant and perform the reaction at a higher temperature than the

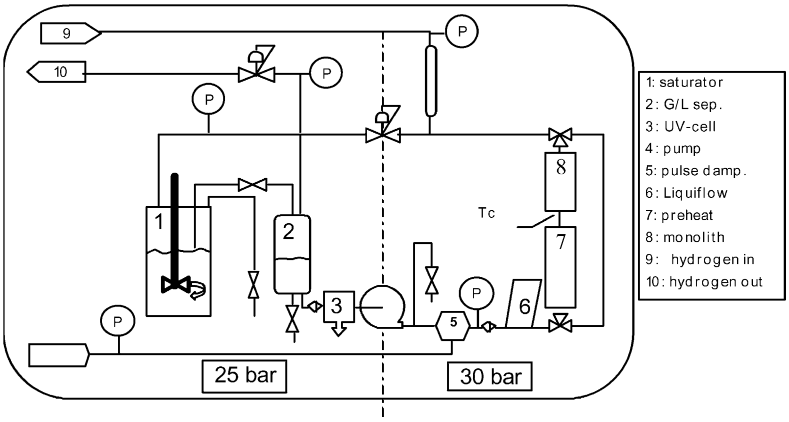

Fig. 1. Monolith test reactor.

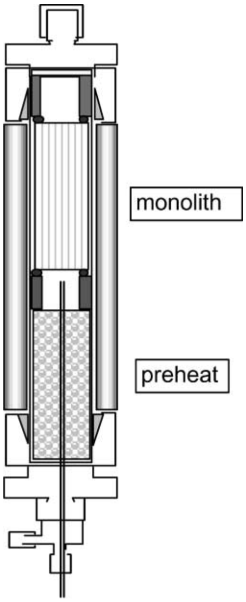

Fig. 2. Reactor with monolith and pre-heat section.

saturation. As hydrogen solubility increases with temperature [4], this ensures that any remaining gaseous hydrogen is dissolved before reaching the monolith. The design was also checked with liquid saturated at 1 bar and a glass tube at the place of the reactor at 6 bar (g). No gas bubbles were observed.

Hydrogenation of tetralin was performed using a mixture of 2 wt.% tetralin and 98 wt.% terpentina D. Conversion of aromatics was measured in-line with a fiber optic spectrometer at UV-274 nm wavelength. An high pressure TEE-union was equipped with an high temperature absorbance dip probe with adjustable pathlength.[1] Furthermore, liquid samples were taken and analyzed by gas chromatography. The tethered monolith was exposed to a 1% 1-hexene in methanol solution saturated with hydrogen. Analysis of liquid samples was carried out by gas chromatography.

The high pressure membrane pump had a maximum capacity of $1.3\,\mathrm{l\,h^{-1}}$. Thus creating a linear velocity of $0.6\,\mathrm{m\,h^{-1}}$ through the monolith. With an effective monolith volume of $28 \times 10^{-3}\,\mathrm{l}$, this means that the maximum liquid hourly space velocity (LHSV) was $46\,\mathrm{h^{-1}}$. The average feed volume was 0.7 l.

The monolithic catalysts were prepared using conventional techniques. A cordierite monolith with 400 cpsi was washcoated with alumina on which the catalytically active metal or the homogeneous catalyst was deposited. The catalysts were activated in situ using downflow hydrogen.

3. Results and discussion

Fig. 3 shows the observed decrease in aromatics content during the very first experiment with the equipment. At 50°C, the Pd-loaded monolith showed little activity, but the temperature increase to 110°C boosted hydrogenation. This demonstrated the concept.

Next an experimental design program was setup to determine the effect of several process parameters on the performance of the unit. The temperature of the reactor was held constant at 110°C, since an increase in catalyst activity with temperature was already demonstrated.

Increasing the pressure in both the saturation and reaction part of the unit had a positive influence on the hydrogenation rate. This means that the reaction had an order in hydrogen. Since no gas phase is present, this obviously relates to the hydrogen solubility. A higher pressure difference between the saturation and reaction section had a negative influence on the reaction rate. In other words, dissolving less hydrogen in the liquid decreased the hydrogenation rate, again indicating that the reaction had an order in hydrogen.

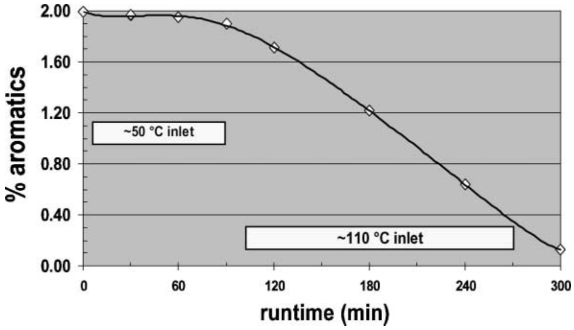

Fig. 3. First hydrogenation trial with Pd-monolith using a 2% tetralin/terpentina feed.

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[1] Special design from TOP sensor systems. Path adjustable between 0.1 and 10 mm.

The liquid flux showed no influence on the overall system hydrogenation rate. With an higher LHSV, a lower conversion per pass would be expected. This was confirmed by GC analysis. The lower conversion per pass is counterbalanced by the increased number of passes per hour resulting in equal overall system hydrogenation rate. So, the flux does not influence the productivity of the system. Except in the case of a too low flux where the limitation in hydrogen solubility becomes evident.

All hydrogenation test runs behaved according to a pseudo-zero order kinetics (see Fig. 3). However, in the experimental design, the aromatic concentration showed a slightly positive influence on the reaction rate. This contradiction has not been explored further.

In a separate set of experiments, the maximum tetralin hydrogenation rate was measured to be $23.7\,\mathrm{mmol\,h^{-1}}$ at a saturation temperature of 25°C and 25 bar with a liquid flux through the monolith of $1.02\,\mathrm{l\,h^{-1}}$. From these numbers, the hydrogen consumption at these conditions was calculated to be $70\,\mathrm{mmol\,h^{-1}\,l^{-1}}$. This consumption is lower than the reported solubility of hydrogen in heptane at 1 bar pressure ($0.71\,\mathrm{mol\,l^{-1}}$) [4], suggesting that the reaction is limited by catalyst activity. However, a further increase in reactor temperature resulted in significant irreversible catalyst deactivation, which was attributed to coke deposition on the catalyst.

In literature, the effectiveness of a monolith is considered to be very high since internal mass transport limitations are minimized due to its open structure and the thin washcoat. An experiment was carried out to verify this. A Pd-monolith was milled ($<150\,\mu\mathrm{m}$) and an equal amount was taken as compared to the effective monolith area in the test (28 ml = 14.9 g). A autoclave test with this powder at 25 bar and 120°C was performed. The observed average hydrogenation rate was $21\,\mathrm{mmol\,h^{-1}}$. Compared to the $17\,\mathrm{mmol\,h^{-1}}$ at 110°C (converted to $21\,\mathrm{mmol\,h^{-1}}$ at 120°C) means indeed an effectiveness of ~100%.

The activity of different monolith loaded with Pd or Ni (as described in Table 1) were compared in the tetralin hydrogenation reaction. At 110°C, the Ni-monolith showed a four times lower activity compared to the Pd-loaded monolith. This is attributed to a lower dispersion of the Ni catalyst as it has equal or higher intrinsic activity than Pd for the hydrogenation of aromatics [5].

Table 1
Tested monoliths

Code	Metal	Washcoat	Feedstock
C116	1% Pd	Alumina	2% tetralin
C561	1% Ni	Alumina	2% tetralin
Q310	0.032% Rh	Proprietary	1% hexene

To broaden the usability of the two-phase hydrogenation system, the hydrogenation of 1-hexene with a homogeneous Rh-cyclooctadiene-1,2-bis-diphenylfosfino-ethane catalyst that was tethered to the monolith was tested. The solvent used was methanol. A zero-order hexene hydrogenation rate of $9\,\mathrm{mmol\,h^{-1}}$ was measured. Since only 0.078 mmol Rh was present, this means a TOF of 115 mol hexene per mole of metal per hour. The tests also revealed that the oxygen sensitivity of the catalyst did not change upon tethering it to the monolith.

4. Conclusions

It was shown that dissolved hydrogen can be used to carry out hydrogenations of aromatics and/or olefins. The ability to separate the reaction and the dissolving of hydrogen allows for a simple process design that uses an autoclave to saturate the feed with hydrogen and a catalyst coated on a monolith to facilitate the reaction.

Besides catalyst activity, the solubility of hydrogen was the most important parameter that affected the hydrogenation rate. The effectiveness of the (Pd)-monolith was found to be 100%.

Tethering of homogeneous catalysts on the monolith allows (fine)chemical producers to repeatedly use the expensive homogeneous catalysts without the need for separation of the catalyst from the reaction mixture.

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