



Modeling of monolithic and trickle-bed reactors for the hydrogenation of styrene

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Abstract

A kinetic study into the styrene hydrogenation over a palladium on alumina catalyst has been made. Styrene was used as a model component for pyrolysis gasoline. A kinetic rate expression has been derived and the inhibiting effect of sulfur components has been included. Using this kinetics and mass-transfer models compiled from literature, the performance of two types of reactors for the styrene (pyrolysis gasoline) hydrogenation has been evaluated. A structured reactor such as a monolith has large advantages over a conventional trickle-bed reactor. For the monolithic reactor a more than 3 times higher volumetric productivity is obtained with much less catalyst. The modeling results indicate that deactivation by gum formation should be significantly less due to much better hydrogen mass transfer in the reactor.

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1. Introduction

The hydrogenation of styrene was chosen as a model reaction for the industrially widely applied hydrogenation of pyrolysis gasoline. Pyrolysis gasoline (PYGAS) is one of the product streams from the thermal decomposition of heavier oil fractions. This thermal decomposition is mainly carried out for the ethylene and propylene production. Typical PYGAS contains C₅–C₁₂ hydrocarbons. Among these hydrocarbons there are typically up to 15 wt% of gum-forming agents, mostly diolefins and styrenes. To prevent gum-formation in later processes or during storage, these reactive molecules need to be hydrogenated. PYGAS also contains different olefins and aromatics which are much less reactive and therefore need not be hydrogenated. Styrene was chosen as the model component to be hydrogenated since this is one of the slower reacting components which should be removed. The sulfur content of PYGAS typically ranges from 5–500 ppm, depending on the origin. An average value is 100 ppm and consists for the major part of thiophene (typically > 50%) and methylthiophene (typically 20%). To a much lesser extent (only up to a few

per cent) more poisonous mercaptanes (e.g. ethanethiol) can be present. Some general information on the PYGAS hydrogenation can be found in the paper by Cheng, Chang and Wu (1986).

In this paper first a kinetic study into the styrene hydrogenation is described and the different parameters which affect the reaction rate. Subsequently, this kinetic information is used for a model-based comparison between the conventionally used trickle-bed reactor and a monolithic reactor for the hydrogenation of a model PYGAS of styrene and thiophene in toluene.

2. Experimental

The kinetic experiments were performed in a batch-autoclave slurry reactor. A 500 ml Zipperclave from Autoclave Engineers was used for these experiments. This reactor contained two baffles and a gas-inducing Rushton-type stirrer, typically operated at 1500 rpm. The autoclave was electrically heated using a heating jacket. To better control the temperature of the reactor a continuous stream of cooling water was fed at about 1.5 l/min through a coil in the autoclave. The pressure in the autoclave was controlled using an electronic forward-pressure controller. The

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gas consumption during the experiments was measured by an electronic mass-flow meter, connected to a flow-totalizer box.

Catalytic tests were performed using an Engelhard H5426U 0.5 wt% palladium on alumina catalyst and one other different commercial 0.4 wt% palladium on alumina catalyst. Both catalysts were highly dispersed Pd on alumina catalysts with a BET surface area of about 100 m²/g. The catalysts were in their original shape spherical with the palladium located in a thin egg-shell. The catalysts were milled and sieved to different particle size fractions of < 20, 20–40 and 40–100 μm. The experiments were conducted by putting typically 80 mg of the catalyst (dried overnight at 393 K) in the autoclave reactor, together with 160 g of toluene. The catalysts were subsequently reduced at 398 K and 5 bar hydrogen pressure for 1.5–2 hours at a 500 rpm stirring rate. The reactor was allowed to cool down to the reaction temperature (typically 323 K), after which the feed was added from a liquid feed vessel. The liquid feed was typically 30 g of styrene (of which the *t*-butylcatechol inhibitor had been removed) in 100 g of toluene. The stirrer was set to 1500 rpm and the reactor pressure (typically 16 bar) was applied. During the course of the experiment regularly liquid samples were taken, at which time temperature, pressure and hydrogen consumption were recorded. During the startup of the experiment the unit was first flushed with nitrogen to remove all air from the system and thereafter flushed 3 times with hydrogen to remove all nitrogen from the system. The liquid samples were analyzed using a Perkin-Elmer Autosystem gas chromatograph equipped with FID detector and autosampler. A J&W DB-1 column (60 m × 0.25 mm, 1 μm film, 1 ml/min He flow) was used with a temperature program (1 min 353 K isothermal, heating 5 K/min to 473 K, 1 min isothermal).

3. Results and discussion of kinetics

An example of a typical styrene hydrogenation experiment is shown in Fig. 1. The hydrogen consumption corresponds well to the styrene conversion. The reaction initially proceeds via a 0-order in styrene and changes to a first order when complete conversion is being approached. This indicates a Langmuir–Hinshelwood-type kinetic model.

3.1. Effect of stirring rate and catalyst

Experiments performed at 1000 and 1500 rpm stirring rate showed an identical reaction rate, indicating that hydrogen dissolution were not limiting the reaction. Experiments using different amounts of catalyst showed a first-order behavior in the catalyst concentration, which confirms that hydrogen dissolution was not limiting.

Experiments have been performed with different size catalyst particles (20–40 and 40–100 μm). The activity obtained with the smaller particles was approximately 25% higher

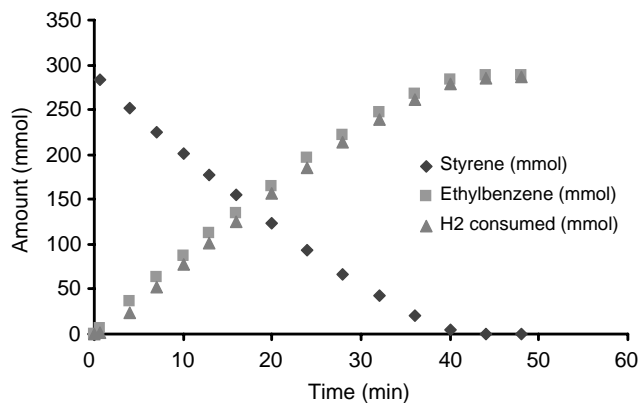


Fig. 1. Example of a typical styrene hydrogenation experiment in batch slurry autoclave. (catalyst A, 17 bar H₂, 323 K, 0.19 g catalyst/l (40–100 μm), initial styrene 0.86 mol/l).

than that of the larger catalyst particles, which indicates that there is some extent of internal mass-transfer limitation occurring for the larger particles.

The catalysts from the different suppliers all give similar activities once the activities were normalized for the palladium loading. The effects of varying operational parameters of these catalysts was also similar. Experiments in which the *t*-butylcatechol was not sufficiently removed by filtering the styrene over alumina showed a lower activity, indicating the importance of this filtering step.

3.2. Effect of temperature

Experiments have been performed at different temperatures at a total pressure of 6 bar. Using the initial rates from these experiments an Arrhenius-plot has been constructed to determine the apparent activation energy of the reaction. The Arrhenius-plot is given in Fig. 2. The rates in this figure have been corrected using a first-order assumption for the decreasing hydrogen pressure as a result of an increasing

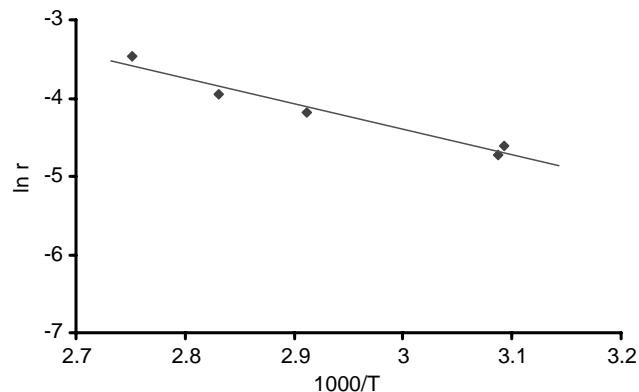


Fig. 2. Arrhenius-plot for the hydrogenation of styrene in toluene. Initial styrene hydrogenation rates (mol/g.catalyst/min/barH₂) versus reciprocal temperature. Catalyst A, styrene concentration 0.86 mol/l, catalyst (40–100 μm) 0.2 g/l, 6 bar total pressure.

vapor pressure with temperature. The apparent activation energy amounts to 27 kJ/mol. For the styrene hydrogenation over Pd catalysts activation energies have been reported of 15 kJ/mol by Cheng et al. (1986), 41 ± 8 kJ/mol by Jackson and Shaw (1996), and 55 kJ/mol by Chaudhari, Jaganathan, Kolhe, Emig, and Hofmann (1986). The value of 15 kJ/mol seems unrealistically low. The value calculated from Fig. 2 is most likely influenced by internal mass-transfer effects, considering the effect of the particle size on the reaction rate discussed in the previous section. If internal mass-transfer controls the reaction, the true activation energy is half the observed activation energy (Scott Fogler, 1999). Consequently the observed activation energy of 27 kJ/mol would indicate a true activation energy of 54 kJ/mol, which is in good agreement with the last two reported values. The observed activation energy of 27 kJ/mol makes external mass-transfer limitations unlikely, since in that case the observed activation energy should have been lower than 10 kJ/mol.

3.3. Effect of pressure

Experiments were performed at different hydrogen pressures to determine the reaction order for the reaction in hydrogen (Fig. 3). It can be seen that for the Engelhard catalyst at a pressure of up to 20 bar the reaction shows a first order behavior in hydrogen. This type of behavior was anticipated and is common for hydrogenation reactions. At higher hydrogen pressures the reaction rate levels off. This leveling off also occurred for the other catalysts tested. Commonly such a behavior can be described by a Langmuir–Hinshelwood behavior of hydrogen on the catalyst surface (in that case the reaction rate no longer increases once the catalyst surface is fully occupied with hydrogen). Fitting such Langmuir–Hinshelwood expressions to the observed pressure dependency did not produce acceptable results. The transition from first order behavior to a constant reaction rate proved to be

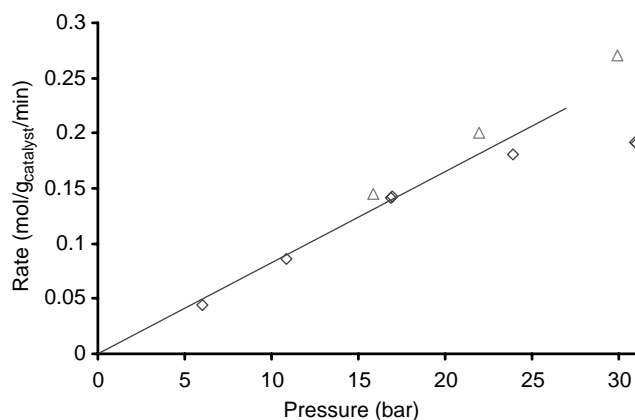


Fig. 3. Styrene hydrogenation performed at different hydrogen pressures. Shown are the initial styrene conversion rates at 323 K, styrene concentration 0.86 mol/l: (◇) Engelhard H5426U catalyst, 20–40 μm 0.24 g/l; (△) commercial catalyst C, 36–63 μm , 0.24 g/l measured in different test reactor.

too abrupt to be able to be described by such an expression. Since it was likely that at the high pressures the gas supply system was limiting the reaction, some experiments were conducted elsewhere in a different autoclave reactor. These experiments using a similar palladium catalyst did show a first-order behavior at a pressures above 20 bar. The first order behavior with respect to the hydrogen pressure on the styrene hydrogenation rate was also found by Chaudhari et al. (1986). It is therefore concluded the reaction is first order in hydrogen up to a pressure of at least 30 bar.

3.4. Sulphur inhibition

Experiments have been performed with thiophene concentrations from 0 to 800 ppm (Fig. 4). It can clearly be seen that thiophene has a strong inhibiting effect on the catalyst. For both catalysts used the inhibiting effect is similar. The experiments shown in Fig. 4 are normalized for the amount of palladium to account for the different metal loadings for the two catalysts. The line drawn is of a single-site Langmuir–Hinshelwood expression fitted to the experiments to describe the inhibiting behavior of thiophene. It was found that this type of inhibition described the observations best.

An experiment with 30 ppm of ethanethiol (ethylmercaptane) was also carried out. This experiment is also shown in Fig. 4. This component, present in minor amounts in PY-GAS, has an even stronger inhibiting behavior on the styrene hydrogenation. It can be estimated from this observation that the adsorption of ethanethiol is about 10 times stronger than that of thiophene. Since mercaptanes like ethanethiol are present in PYGAS only in amounts of a few percent in total (their boiling point is very low compared to PYGAS), this means that the overall inhibiting contribution of these components will be smaller than that of the thiophenes, but not negligible.

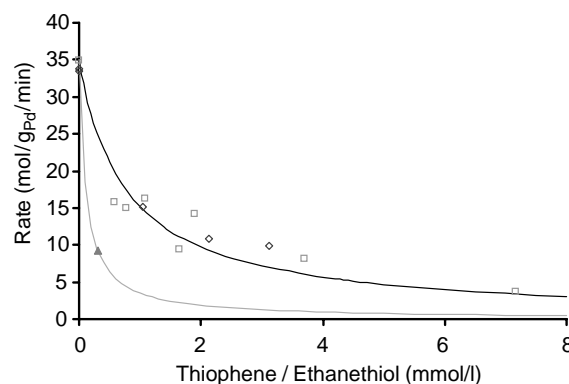


Fig. 4. Initial reaction rate as a function of the amount of sulfur component present in the feed (0.86 mol/l styrene, 17 bar hydrogen pressure, 323 K, 20–40 μm catalyst particles). (□) catalyst A thiophene; (◇) thiophene Engelhard H5426U catalyst; (▲) ethanethiol Engelhard H5426U catalyst. Lines: Langmuir–Hinshelwood inhibition fits for thiophene (black) and ethanethiol (gray).

3.5. 1-Octene experiments

An example of a 1-octene hydrogenation experiment is shown in Fig. 5. The hydrogenation rate towards octane is considerably slower than the hydrogenation of styrene (approximately 40 vs. 140 mmol/g_{catalyst}/min). Furthermore, as a side reaction a considerable amount of octene isomerization occurs at a similar rate. In a competitive hydrogenation experiment between styrene and 1-octene (Fig. 6) the 1-octene reaction is effectively blocked by the styrene, which can be explained by a much stronger adsorption of styrene compared to 1-octene in a Langmuir–Hinshelwood kinetic model. Smits, Stankiewicz, Glass, Fogl, and Moulijn (1996) report the same reactivity behavior for the hydrogenation of a styrene–1-octene mixture. Since olefin hydrogenation is not preferred in the PYGAS hydrogenation reactor, this type of behavior of the catalyst is desired.

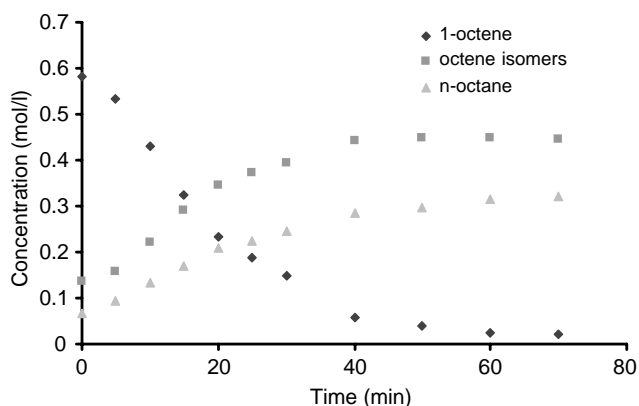


Fig. 5. 1-Octene hydrogenation. (slurry, catalyst A, 16 bar, 323 K, 0.79 mol/l 1-octene, 0.21 g_{catalyst}/l).

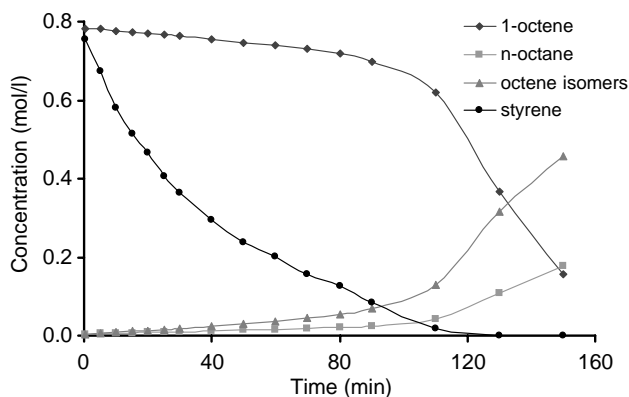


Fig. 6. Competitive hydrogenation with styrene and 1-octene (slurry, catalyst A, 16 bar, 323 K, styrene 0.85 mol/l, 1-octene 0.79 mol/l, catalyst 0.21 g/l).

4. Kinetic modeling

The kinetic experiments were modeled using the Athena Visual Workbench package (v. 8.0, Stewart & Associates Engineering Software). Based on the observations a first order in hydrogen, 0 to first order in styrene and –first order in thiophene the following Langmuir–Hinshelwood rate equation was utilized:

$$r = kC_{H_2} \frac{K_{sty}C_{sty}}{1 + K_{sty}C_{sty} + K_{thio}C_{thio}}$$

Other types of kinetic rate expressions were also investigated, but did not produce satisfactory results. In the kinetic expression used the hydrogen concentration is in a separate term from the Langmuir–Hinshelwood term for the organic components, which implies that hydrogen adsorption is possibly independent of the organic molecules at different adsorption sites. The first order in hydrogen indicates that the hydrogen occupancy remains low. Neither adsorption of toluene nor adsorption of ethylbenzene are present in the kinetic expression. This can be rationalized by an assumption that either their adsorption term is negligible in the denominator of the Langmuir–Hinshelwood term or, in the case of toluene, that the toluene adsorption term has ‘disappeared’ into the 1 in the denominator, which is possible since the toluene concentration was constant.

For the modeling of the slurry reactor the following expressions were utilized: Differential equations for the catalysts particles:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial z^2} + \frac{2}{z} \frac{\partial C}{\partial z} \right) - r.$$

Equations solved in spherical coordinate system (with radius z), for both hydrogen and styrene (each with their appropriate diffusivity). The corresponding boundary conditions are

$$z = 0, \quad \frac{\partial C}{\partial z} = 0$$

$$z = r_p, \quad C = C_{bulk}$$

For hydrogen the bulk concentration is assumed to remain saturated. For the bulk concentration of styrene the following differential equation was utilized:

$$\frac{\partial C_{sty,b}}{\partial t} = - \frac{3}{r_p} \frac{C_{cat}}{\rho_{cat}} D_{sty} \frac{\partial C}{\partial z} \Big|_{z=r_p}$$

With for all equations as starting values:

$$t = 0, \quad C_{H_2} = C_{H_2,sat}, \quad C_{sty} = C_{sty,0}$$

The differential equations were fitted to the experimental observations. The parameters that were fitted to the experiments are: k , K_{sty} , and K_{thio} . The diffusion coefficients for styrene and hydrogen were estimated using the approximation method of Wilke and Chang (1955). A set of five experiments was chosen which were modeled simultaneously to determine the rate parameters for each model. For one single

Table 1
Modeling results for fitting kinetic model a representative set of experiments (323 K).

Parameter	Optimal estimate	95% confidence interval	
		Lower	Upper
k (1/min)	2010	1680	2330
K_{sty} (l/mol)	13.3	10.2	16.3
K_{thio} (l/mol)	15310	12800	17800

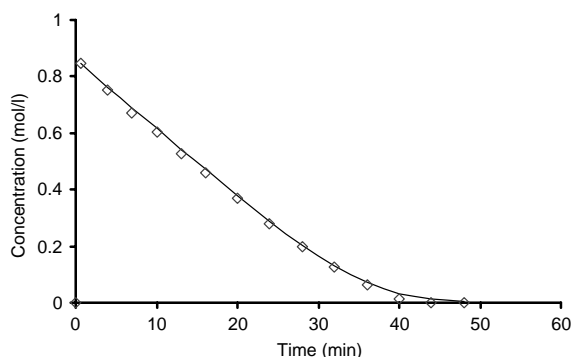


Fig. 7. Measured (markers) and modeled (line) concentrations over time for a styrene hydrogenation experiment (catalyst A (20–40 μm) 0.14 g/l, 323 K, 16 bar).

temperature and pressure (323 K and 17 bar of hydrogen) the equations were fitted to an experimental set containing two experiments with different catalyst particle sizes without thiophene present and three experiments with different thiophene concentrations. No attempts have been made so far to simultaneously fit experiments at different temperatures and pressures, since this greatly complicated the fitting process due to the increased number of parameters and more complex mathematics in that case. The separately determined effect of temperature (apparent activation energy) and pressure (first order in hydrogen) were directly incorporated in the model instead. Using an apparent activation energy was deemed allowable considering the relatively mild adiabatic temperature rise of 20°C in the full-scale reactors modeled. The parameters fitted to the experiments are given in Table 1. An example of the adequateness of the fits is given in Fig. 7. The model describes the experiments well.

5. Reactor modeling

Using the kinetics determined in the batch-slurry autoclave reactor and information on mass transfer from literature, the performance of a full-scale trickle-bed and monolithic reactor has been modeled. These modeling calculations have also been performed with the Athena Visual Workbench package. The modeling was done for a simulated PYGAS feed containing 5 wt% of styrene to be hydrogenated and 200 ppm of thiophene in the feed. The industrial feed

typically contains 5–500 ppm sulfur and 15 wt% styrene. The liquid feed is assumed to be saturated with hydrogen. To prevent excessive temperature rises by the heat of reaction typically recycle ratio's between 1 and 3 are used in industrial PYGAS hydrogenation processes, making the conditions chosen for these calculations realistic conditions. The inlet temperature was assumed to be 323 K and the reactor pressure 15 bar. Included in both models are

- different mass-transfer steps (will be specified for each model separately),
- depletion of the hydrogen in the gas phase and thereby a decreasing gas stream,
- temperature effects by the heat liberated by the reaction (adiabatic temperature rise: approximately 20°C). Taken into account for gas density, rate constants, vapor pressures, diffusivities, and viscosity,
- increase in gas phase by evaporation of organics (toluene),
- catalyst effectiveness factors by means of Thiele moduli are calculated to account for mass-transfer inside the catalysts. First-order approximations were used for the Thiele modulus for the component most limiting (i.e. for which the diffusivity multiplied by the driving force was smallest—hydrogen in the first part of the reactor and styrene once near complete conversion).

The catalyst effectiveness using the Thiele modulus was calculated for the transport distance into the catalyst that was of relevance, i.e. for the eggshell thickness of the trickle-bed catalyst and the thickness of the washcoat layer for the monolithic catalyst. Translating the intrinsic activities determined from the slurry experiments into intrinsic activities of the trickle-bed and monolithic catalyst was done by assuming the intrinsic rates were the same when normalized per amount of palladium on the catalyst.

5.1. Trickle-bed reactor

A typical industrial trickle-bed reactor for the PYGAS hydrogenation is operated at a superficial velocity of typically 0.01–0.03 m/s. In the modeling calculations a velocity of 0.02 m/s has been used. The gas feed is commonly stoichiometric with some amount of excess. In the modeling a 50% excess for hydrogen was used. In Table 2 the reactor parameters for the calculations are given. For the trickle-bed catalyst all palladium is assumed to be present in a thin eggshell layer of the catalyst particles, for the monolithic catalyst all palladium is assumed to be present in the alumina wascoat-layer coated on the monolith.

The trickle-bed mass-transfer model was based on the model discussed by Rajashekharam, Jaganathan, & Chaudhari (1998). A schematic representation of the model is given in Fig. 8. Catalyst particles are surrounded by a dynamic liquid zone, a static liquid zone, and a dry zone. The dynamic liquid is assumed to move down through

Table 2
Reactor parameters used for modeling of monolith and trickle-bed reactors

	Trickle-bed	Monolith
Pressure (bar)		15
Liquid inlet temperature (K)		323
Styrene (mol/l)		416
Thiophene (ppm)		200
Particle size (mm)	3	
Eggshell thickness (μm)	100	
Cell density (cpsi)		400
Washcoat loading (wt%)		20
Pd on catalyst / washcoat (wt%)	0.4/-	0.16/0.8
Bed (structure) porosity (dimensionless)	0.4	0.64
Superficial liquid velocity (m/s)	0.02	0.1
Superficial gas velocity (m/s)	0.067	0.32

the reactor uniformly at the superficial velocity specified. Mass-transfer exchanges styrene and hydrogen between the zones. External mass-transfer for both hydrogen and styrene to the catalyst particles is taken into account. In the model it is assumed that the styrene concentration on/in the particle is uniform, so also in the dry-zone of a partially wetted catalyst particle the reaction is able to proceed at a significant rate. In practice this is only possible for partially wetted particles. This assumption, therefore, does imply that the calculated reactor performance is somewhat better than it will be in practice where also completely dry particles in the reactor are a possibility. Separate catalyst effectiveness factors are calculated for the catalyst particles in each of the zones, since the hydrogen concentrations on the catalyst particles are different at these different locations.

The equations used for modeling the concentration profiles in trickle-bed reactor are given in Scheme 1.

The results of the modeling calculations are shown in Fig. 9 for a trickle-bed reactor operating at a pressure of 15 bar. It can be seen that the hydrogen concentrations at the catalyst are very low because of the slow transport (diffusion) process through the stagnant film surrounding the catalyst particles.

It can be seen that the reactor has three zones:

- a hydrogen mass-transfer limited zone (almost constant low hydrogen concentration on the catalyst, 0th order in styrene),
- a styrene mass-transfer limited zone (hydrogen concentration on catalyst starts increasing, first order in styrene)
- a kinetically limited zone (slow reaction, hydrogen on catalyst close to saturated, first order in styrene)

The bulk of the conversion takes place in the hydrogen mass-transfer limited zone (the first approximately 1.8 m of the trickle-bed reactor in Fig. 9), and therefore this zone is most important for designing an industrial PYGAS hydrogenation reactor. An important factor in the PYGAS hydrogenation is the gum-formation on the catalyst by which it loses activity. It is most likely that in this first zone, where the amount of hydrogen on the catalyst is very low, gum-formation is most severe.

The second styrene mass-transfer limited zone and the third kinetically limited zone are less relevant to the real-life situation. When a real PYGAS feed is used this contains olefins that should not be hydrogenated. In a reactor these components will start reacting once the styrenes and similarly reactive components are no longer present in sufficient amounts. The modeling calculations are therefore no longer comparable to the industrial practice once the conversion of styrene surpasses about 90%.

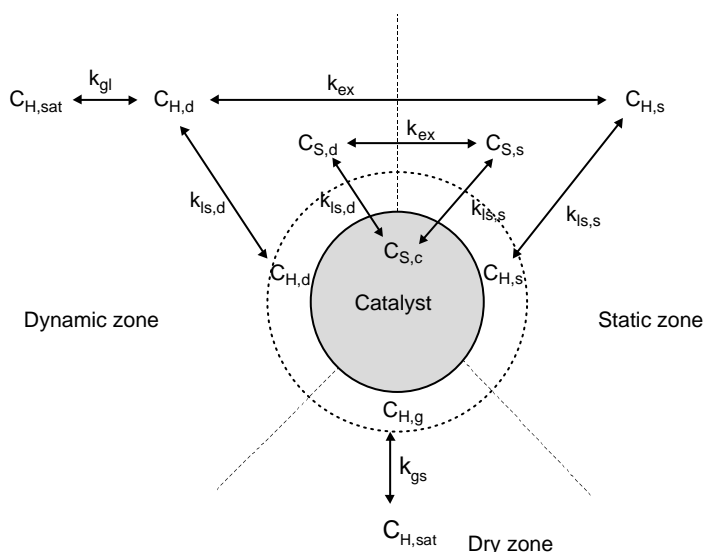


Fig. 8. Schematic representation of mass-transfer model used for the description of the trickle-bed reactor. (based on Rajashekaram et al. (1998)).

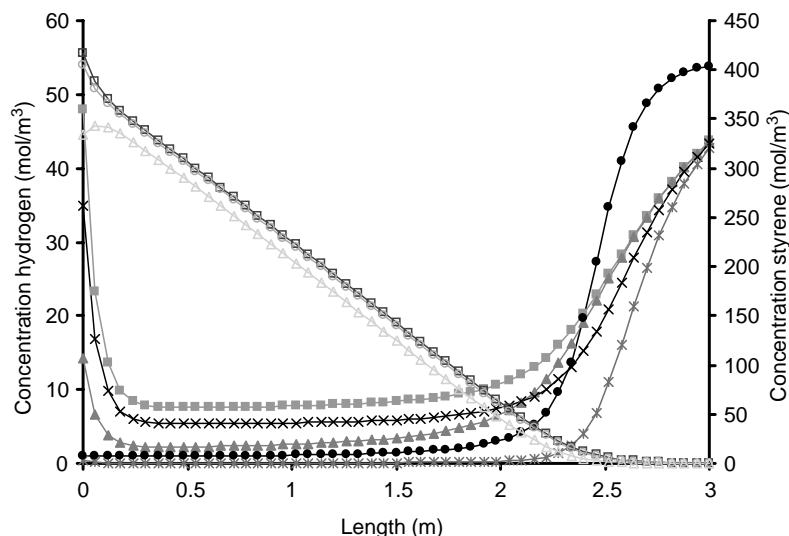


Fig. 9. Modeling results for trickle-bed reactor for the PYGAS hydrogenation at 15 bar: (■) Hydrogen concentration in dynamic liquid (mol/m^3); (▲) Hydrogen concentration in dynamic liquid at catalyst (mol/m^3); (×) Hydrogen concentration in stationary liquid (mol/m^3); (*) Hydrogen concentration in stationary liquid at catalyst (mol/m^3); (●) Hydrogen concentration at catalyst in dry zone (mol/m^3); (□) Styrene concentration in dynamic liquid (mol/m^3); (○) styrene concentration in static liquid (mol/m^3); and (△) styrene concentration at catalyst (mol/m^3).

5.2. Monolithic reactor

A monolithic reactor has to operate at different conditions than a trickle-bed reactor. To operate a monolithic reactor with two-phase-flow in a hydrodynamically stable regime (Taylor-flow), superficial gas and liquid velocities of at least 0.1 m/s are required (Grolman, Edvinsson, Stankiewicz, Moulijn (1996)). Operating at lower velocities results in maldistribution of gas and liquid in the reactor since liquid falls down rapidly due to gravity. To enable an easy comparison with the trickle-bed reactor the lower values for the operating regime are used to model the monolith reactor. Operating a trickle-bed reactor at these high velocities is not possible because of the high pressure drop that would then be encountered.

Taylor flow in a monolithic reactor can be easily modeled. With this flow type the monolithic wall is continuously wetted by a liquid film. Through the channels travel gas bubbles and liquid slugs (Fig. 10). The liquid movement through the channels causes internal circulation to occur in the liquid slugs, allowing for the simplification to assume these slugs to be ideally mixed. More information on this flow type in a monolithic channel can be found in Edvinsson and Irandoust (1996).

In the model for the monolithic reactor all external mass-transfer steps for both hydrogen and styrene are taken into account. The schematic representation of these individual mass-transfer steps are depicted in Fig. 10. For the styrene mass-transfer from the bulk of the liquid (the slugs) to the catalyst surface is considered. For hydrogen both 'direct' mass-transfer from the gas bubbles through the thin liquid film to the catalyst surface and indirect mass-transfer from the gas bubbles via the liquid slugs to the catalyst

surface are taken into account. To account for internal diffusion limitations catalyst effectiveness factors by means of Thiele moduli are calculated.

The model used for modeling the monolithic reactor has been developed by Kreutzer, Du, Heiszwolf, & Moulijn (2001). The model is given in Scheme 2.

The results of solving these differential equations are shown in Fig. 11. It can be seen that, although mass-transfer to the catalyst is somewhat limiting the reaction rate, the mass-transfer rates are close to the kinetically controlled rates, since the styrene and hydrogen concentrations near the catalyst surface are close to the bulk concentrations.

5.3. Comparison

When the monolithic and the trickle-bed reactor are compared, it can be seen that the monolith needs about 30% longer reactor length to achieve complete conversion of all styrene in the feed. However, for the monolithic reactor the throughput of the liquid is five times higher than for the trickle bed. That the monolithic reactor is able to convert more liquid in the same size reactor can be explained by the much more efficient mass-transfer. As a result of the more efficient mass-transfer the hydrogen concentration at the monolithic catalyst is significantly higher than that at the trickle-bed catalyst (34 instead of $2.2 \text{ mol}/\text{m}^3$). This higher hydrogen concentration at the catalysts makes that the catalyst is utilized much more effectively. The higher effectivity of the monolithic catalyst is further illustrated by the fact that the monolithic reactor is able to achieve the over three times higher productivity with 75% less active catalyst material (Pd) in the reactor (see Table 3). The absence of dry

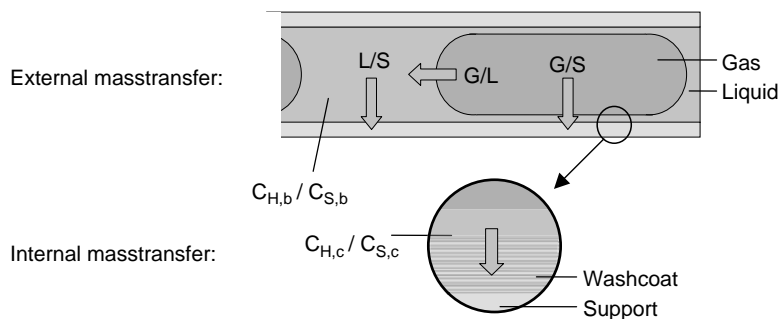
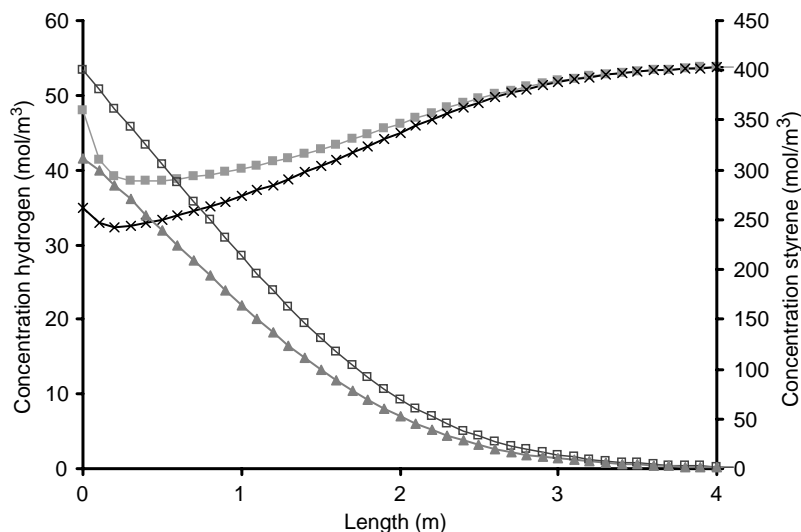


Fig. 10. Schematic representation of the mass-transfer steps in a monolithic reactor.

Fig. 11. Modeling results for a monolithic reactor at 15 bar for the PYGAS hydrogenation; (■) Hydrogen concentration in bulk liquid (mol/m^3); (×) Hydrogen concentration in liquid at catalyst (mol/m^3); (□) Styrene concentration in bulk liquid (mol/m^3); (▲) Styrene concentration at catalyst (mol/m^3).Table 3
Comparison between reactor types (at 15 bar, calculated)

	Trickle-bed	Monolith
Productivity ($\text{m}^3_{\text{feed}}/\text{m}^3_{\text{reactor}}/\text{h}$) ^a	28	99
Hydrogen on catalyst (mol/m^3) ^b	2.2	34
Active material in reactor ($\text{kg}_{\text{Pd}}/\text{m}^3_{\text{reactor}}$)	3.6	0.8

^aProductivity converting 99% of styrene.^bFor monolith: lowest value on catalyst in reactor, for trickle-bed: lowest value for hydrogen concentration in dynamic zone on catalyst (highest value of the three zones)

or stagnant liquid zones in the monolithic reactor is also an advantage, since all of the catalyst in the reactor is thereby being used and not subjected to different conditions.

An added advantage for the monolithic reactor is that one would expect that the catalyst deactivation by gum formation on the catalyst would be much less for the monolithic catalyst, since gum-formation is prevented by a larger hydrogen concentration on the catalyst (Moulijn, Makkee, & van Diepen, 2001). Deactivation by other causes (poisons in feed) might be higher for the monolithic reactor, since the

amount of catalyst in this reactor type is less. However, this can be solved easily by using a relatively high metal loading on the monolithic catalyst to obtain a similar Pd-loading in both reactor types. In Table 3 the relevant numbers for the different reactors are summarized.

Monolithic and trickle-bed reactors cannot be operated at the same hydrodynamic conditions. A trickle-bed cannot be operated at the high flowrates at which a monolith is used because of pressure-drop considerations. The monolithic reactor needs high superficial velocities to be able to operate hydrodynamically stable. Increasing the gas and liquid flowrates of the trickle bed reactor in the model to the trickle bed unrealistic values of the monolithic reactor does increase the productivity of the trickle-bed reactor by a factor of 2.5, which makes it still 30% lower than that of the monolith. This increase is only caused by the increase in liquid flowrate, since the gas flowrate has only a very minor effect on the mass-transfer in a trickle-bed reactor (Rajashekharam et al., 1998). Even though at such conditions the productivity of the trickle-bed would be comparable to that of the monolith, the monolithic reactor can still be expected to easily outperform the trickle-bed, when one considers the

deactivation by gum formation, since the monolithic catalyst will still have a 5 times higher hydrogen occupancy on the catalyst.

A further advantage of the monolithic reactor for the PYGAS hydrogenation is the safety (Kapteijn, Nijhuis, Heiszwolf, & Moulijn, 2001). The PYGAS hydrogenation is an exothermal process ($\Delta H_r \approx 110$ kJ/mol), which is the reason why it is operated as a recycle reactor process. In case a hot-spot is formed in a trickle-bed reactor radial movement of liquid and gas to the hot-spot can cause it to increase. In a monolith with the segregated channels this is not likely. Furthermore, the higher velocities and the absence of stagnant zones make the development of a hot-spot in a monolithic reactor considerably less likely. Should the entire reactor exhibit a temperature excursion, the monolithic reactor can be shut down faster and safer by simply shutting off the liquid feed, since the monolith retains much less liquid than a trickle-bed. Another advantage of the monolithic reactor is that it is much easier to model. This is clear when model schemes 1 and 2 are compared. Uncertainties in the reactor like partial wetting of catalyst particles and completely dry zones are not possible for a monolithic reactor. Although the real situation in the monolith channel is quite dynamic and complex with passing liquid slugs and gas bubbles, it is not necessary to model all the separate bubbles and slugs with a lot of changing boundary conditions at the catalyst. This is true since the liquid film which continuously wets the catalyst dampens out these rapid fluctuations making it possible to operate at close to a quasi steady-state (Edvinsson & Moulijn, 1997).

When monolithic and trickle-bed multiphase reactors are compared one advantage for the trickle-bed reactor is that the gas and liquid-flowrates can be set almost independently, while still maintaining the trickle-flow regime. In down-flow mode, to operate a monolithic reactor hydrodynamically stable in the Taylor-flow regime the liquid fraction in the channels should remain between 20% and 80%, while maintaining a superficial velocity of at least 10 cm/s for both phases. As mentioned earlier, these high velocities are necessary since gravity otherwise pulls down the liquid faster than the desired flowrate, causing maldistribution. When the reactor is operated in upflow-mode this need for high flowrates is not there, but the gas-liquid distribution is more difficult.

A further disadvantage for the trickle-bed reactor is the considerable residence-time distribution in the reactor, caused by the presence of stagnant zones in the reactor. In case where the reaction selectivity is important, this can result in significantly lower selectivities for a trickle-bed reactor in comparison to a monolithic reactor (Nijhuis, Kreutzer, Romijn, Kapteijn, & Moulijn, 2001). The residence time distribution in a monolithic reactor is narrow due to the Taylor-flow patterns, in which the gas bubbles work as pistons separating the liquid slugs preventing backmixing (Thulasidas, Abraham, & Cerro, 1999).

The calculations in this paper clearly demonstrate the advantage of moving to a structured catalyst for a mass-transfer limited reaction system like the PYGAS hydrogenation. Experimental evidence is needed to demonstrate these advantages. A first basis for an experimental comparison between a monolith and a trickle-bed reactor can be found in (Nijhuis et al., 2001) for the very fast alpha-methylstyrene hydrogenation reaction. For this reaction it was demonstrated that the monolith outperformed the trickle-bed due to its better mass-transfer characteristics. The experiments in that paper, however, were performed using a nickel-catalyst, which is less active than the palladium-catalysts used in this paper. Repeating such experiments using a palladium-based catalyst should result in an even larger difference in performance.

Finally, it can be concluded that in case of a faster reaction than the PYGAS hydrogenation modeled in this study the performance of the monolithic reactor will be even better compared to the trickle-bed reactor. For a faster reaction the productivity of the trickle-bed will not go up compared to the productivities modeled in this paper, since for this reaction the trickle-bed catalyst operated in almost the entire reactor in the externally mass-transfer limited regime and, therefore, cannot increase further at these reaction conditions. For the monolithic catalyst the reaction rate was (partially) kinetically controlled and a higher mass-transfer rate is possible for a faster reaction. For example, performing a styrene hydrogenation without sulfur components present would yield even higher (relative) productivities for the monolithic reactor. One such reaction for which this would be the case in a practical application would be the hydrogenation of dinitrotoluene to diaminotoluene. For this process a patent has already been published for the use of a monolithic reactor (Machado, Parillo, Boehme, & Broekhuis, 1999).

6. Conclusions

In the batch-slurry autoclave reactor the kinetics of the hydrogenation of styrene (as a model for PYGAS) over a palladium on alumina catalyst has been determined. The kinetics are of the Langmuir-Hinshelwood type. Sulfur components strongly inhibit the catalyst activity by competitive adsorption. The adsorption strength of thiophene was found to be over 100 times stronger than that of styrene.

Using the kinetic expressions two types of large-scale reactors were modeled. The performance of the catalysts in the currently used industrial trickle-bed reactor is controlled by (external) mass transfer. A numerical comparison between the performance of monolith and trickle-bed reactors for the PYGAS hydrogenation show a clear advantage for using a monolithic reactor. The volumetric productivity of the monolithic reactor is over three times higher than that of the trickle-bed reactor operating at the same pressure and temperature, while the amount of palladium in the monolithic reactor is over four times less. Furthermore, the hydrogen concentration on the monolithic catalyst is significantly

higher than on the trickle-bed catalysts, which is expected to decrease the catalyst deactivation.

Scheme 1. Model for trickle bed reactor

Equations for styrene:

Styrene in dynamic liquid:

$$v_l \frac{\partial C_{S,d}}{\partial z} = -k_{ex} \varepsilon_b (C_{S,d} - C_{S,s}) - f_d k_{ls,d} a_b (C_{S,d} - C_{S,c}).$$

Balance for styrene in stationary liquid:

$$k_{ex} \varepsilon_b (C_{S,d} - C_{S,s}) = f_s k_{ls,s} a_b (C_{S,s} - C_{S,c}).$$

Balance for styrene in catalyst particle:

$$\begin{aligned} f_s k_{ls,s} a_b (C_{S,s} - C_{S,c}) + f_d k_{ls,d} a_b (C_{S,d} - C_{S,c}) \\ = \frac{m_{cat}}{\rho_{cat}} (f_d r_d + f_s r_s + f_g r_g). \end{aligned}$$

Equations for hydrogen (in liquid phase):

Hydrogen in dynamic liquid:

$$\begin{aligned} v_l \frac{\partial C_{H,d}}{\partial z} = k_{gl} a (C_{H,sat} - C_{H,d}) - k_{ex} \varepsilon_b (C_{H,d} - C_{H,s}) \\ - f_d k_{ls,d} a_b (C_{H,d} - C_{H,cd}). \end{aligned}$$

Hydrogen at catalyst in contact with dynamic liquid:

$$k_{ls,d} a_b (C_{H,d} - C_{H,cd}) = \frac{m_{cat}}{\rho_{cat}} r_d.$$

Hydrogen in stationary liquid:

$$k_{ex} \varepsilon_b (C_{H,d} - C_{H,s}) = f_s k_{ls,s} a_b (C_{H,s} - C_{H,cs}).$$

Hydrogen at catalyst in contact with stationary liquid:

$$k_{ls,s} a_b (C_{H,s} - C_{H,cs}) = \frac{m_{cat}}{\rho_{cat}} r_s.$$

Hydrogen at catalyst in contact with gas phase:

$$k_{gs} a_b (C_{H,sat} - C_{H,cg}) = \frac{m_{cat}}{\rho_{cat}} r_g.$$

Reaction rate expressions:

$$r_d = \eta_d \frac{k_r C_{S,c} C_{H,cd}}{1 + K_{sty} C_{S,c} + K_{sulf} C_{sulf}},$$

$$r_s = \eta_s \frac{k_r C_{S,c} C_{H,cs}}{1 + K_{sty} C_{S,c} + K_{sulf} C_{sulf}},$$

$$r_g = \eta_g \frac{k_r C_{S,c} C_{H,cg}}{1 + K_{sty} C_{S,c} + K_{sulf} C_{sulf}}.$$

Heat balance (styrene consumed out of liquid flow is converted to heat):

$$\frac{\partial T}{\partial z} = \frac{-\frac{\partial C_{S,d}}{\partial z} v_l \Delta H_r}{v_l \frac{\rho_l C_{p,l}}{M_l} + v_g \frac{\rho_g C_{p,g}}{M_g}}.$$

Hydrogen flow balance (hydrogen consumed is equal to styrene consumed):

$$\frac{\partial \phi_H}{\partial z} = v_l \frac{\partial C_{S,d}}{\partial z}.$$

Mass-transfer parameters (from Burghardt et al., 1995):

$$\vartheta_z = \left(\frac{\mu_l^2}{g \rho_l^2} \right)^{1/3},$$

$$a_b = \frac{6}{d_p} (1 - \varepsilon_b),$$

$$Re_{zl} = \frac{\rho_l v_l}{a_b \mu_l},$$

$$Re_{zg} = \frac{\rho_g v_g}{a_b \mu_v},$$

$$Ga_m = \frac{d_p}{\vartheta_z} (= Ga_l^{1/3}),$$

$$f_d = 1.125 \left(\frac{a_b d_p}{\varepsilon_b^2} \right)^{0.3} Ga_m^{-0.5} (Re_g + 2.28)^{-0.1},$$

$$\tanh(48.9 Ga_m^{-1.16} Re_l^{0.41})$$

$$f_g = 1 - f_d - f_s,$$

$$Sh_z = (1.19 + 0.0072 Re_{zg})^{1.1} Re_{zl}^{0.494} Ga_l^{-0.22} Sc_l^{0.33},$$

$$k_{ls,d} = \frac{\vartheta_z Sh_l}{D_l}.$$

Parameter estimates

$$k_{ex} = 0.1 Re_l^{0.6}$$

$$f_s = 0.05$$

$$k_{gl} a_{gl} = 0.05$$

$$k_{ls,s} = k_{ls,d}/2$$

$$k_{gs} = 2.5 \times 10^{-5}$$

correlation suggested by Rajashekharan et al. (1998). typical value according to Rajashekharan et al. (1998). high estimate for mass transfer value based on Versteeg, Visser, van Dierendonck, & Kuipers (1992) and Iliuta, Larachi, Grandjean, & Wild (1999).

no data, stationary liquid mass transfer assumed to be same order of magnitude as for dynamic liquid but somewhat slower.

estimate based on Zheng Lu, Smith, Herskowitz (1984).

Scheme 2. Model for monolithic reactor

Styrene in liquid bulk:

$$v_l \frac{\partial C_{S,b}}{\partial z} = k_{ls,s} a_{ls} (C_{S,c} - C_{S,b}).$$

Hydrogen concentration in liquid bulk:

$$v_l \frac{\partial C_{H,b}}{\partial z} = k_{ls,H} a_{ls} (C_{H,c} - C_{H,b}) + k_{gl} a_{gl} (C_{H,sat} - C_{H,b}).$$

Styrene at catalyst:

$$k_{ls,S} a_{ls} (C_{S,b} - C_{S,c}) = r_m \frac{4d_{wc}}{d_c}.$$

Hydrogen at catalyst:

$$k_{ls,H} a_{ls} (C_{H,b} - C_{H,c}) + k_{gs} a_{gs} (C_{H,sat} - C_{H,c}) = r_m \frac{4d_{wc}}{d_c}.$$

Rate expression:

$$r_m = \eta_m \frac{k_r C_{S,c} C_{H,c}}{1 + K_{sty} C_{S,c} + K_{sulf} C_{sulf}}.$$

Heat balance:

$$\frac{\partial T}{\partial z} = \frac{r_m \frac{4d_{wc}}{d_c} \Delta H_r}{v_l \frac{\rho_l C_{p,l}}{M_l} + v_g \frac{\rho_g C_{p,g}}{M_g}}.$$

Hydrogen flow balance:

$$\frac{\partial \phi_H}{\partial z} = -k_{gl} a_{gl} (C_{H,sat} - C_{H,b}) - k_{gs} a_{gs} (C_{H,sat} - C_{H,c}).$$

Mass-transfer parameters (from Kreutzer et al., 2001):

$$L_{slug} = d_h \Psi,$$

$$d_f = d_h 0.18 (1 - e^{-3.08 Ca^{0.54}}),$$

$$a_{gs} = 4(1 - \varepsilon_l)/d_h,$$

$$a_{ls} = 4\varepsilon_l/d_h,$$

$$k_{gs} = \frac{D_{H_2}}{d_f},$$

$$k_{gl} a_{gl} = \frac{0.133 v_s^{1.2}}{L_{slug}^{0.5}} \left(\frac{D_{H_2}}{5 \times 10^{-9}} \right)^{0.5},$$

$$k_{ls,i} = \frac{1}{\frac{1}{D_i/d_h 20 \left(1 + 0.003 \left(\frac{\Psi}{Re Sc} \right)^{-0.7} \right)} + \frac{1}{D_i/d_f}}.$$

Notation

a	mass transfer surface area, m^2/m^3
a_b	geometrical surface area of catalyst bed, m^2/m^3
C_a	Capillary number ($=v_s \eta / \sigma$), dimensionless
C	concentration, mol/m^3
C_p	specific heat, $J/mol/K$
d_c	channel diameter, m

d_f	liquid film thickness, m
d_h	hydraulic diameter (of monolithic channel), m
d_p	catalyst particle diameter, m
d_{wc}	monolithic washcoat thickness, m
D_i	diffusion coefficient of diffusing component in liquid, m^2/s
f_d	catalyst fraction in contact with dynamic liquid, dimensionless
f_g	catalyst fraction in contact with gas (dry), dimensionless
f_s	catalyst fraction in contact with stationary liquid, dimensionless
g	gravitational acceleration, m/s^2
Ga	Gallileo number ($=\rho^2 g d^3 / \mu^2$), dimensionless
Ga_m	modified Gallileo number (see Burghardt, Jaroszynski, & Kolodziej, 1995), dimensionless
ΔH_r	heat of reaction, J/mol
k	mass-transfer coefficient, m/s
k_r	reaction rate constant, $m^3/mol/s$
k_{ex}	exchange coefficient between dynamic and stationary liquid, $/s$
K_{sty}	adsorption equilibrium constant for styrene on catalyst, m^3/mol
K_{sulf}	adsorption eq. constant for sulfur compounds on catalyst, m^3/mol
L_{slug}	liquid slug length, m
M	molar mass, kg/mol
m_{cat}	catalyst concentration $kg/m^3_{reactor}$
r_d	reaction rate at catalyst in contact with dynamic liquid, $mol/m^3_{cat}/s$
r_g	reaction rate at catalyst in contact with gas, $mol/m^3_{cat}/s$
r_s	reaction rate at catalyst in contact with stationary liquid, $mol/m^3_{cat}/s$
r_m	reaction rate in monolithic washcoat layer, $mol/m^3_{cat}/s$
Re	Reynolds number ($=\rho v d / \mu$), dimensionless
Re_z	modified Reynolds number (see Burghardt et al., 1995), dimensionless
Sc	Schmidt number ($=\mu / (\rho D)$), dimensionless
Sh	Sherwood number ($=k d / D$), dimensionless
Sh_z	modified Sherwood for liquid number (see Burghardt et al., 1995), dimensionless
T	temperature, K
v	superficial velocity, m/s
v_s	channel velocity ($=(v_l + v_g)/(1 - \varepsilon_s)$), m/s
z	axial position in reactor, m

Greek letters

ε_b	bed porosity, dimensionless
ε_l	liquid fraction in monolithic channel ($=v_l/(v_l + v_g)$), dimensionless
ε_s	solids fraction of monolithic, dimensionless
η_d	catalyst effectiveness factor catalyst in contact with dynamic liquid phase, dimensionless

η_g	catalyst effectiveness factor catalyst in contact with gas, dimensionless
η_s	catalyst effectiveness factor catalyst in contact with stationary liquid phase, dimensionless
ϑ_z	equivalent length for mass transfer (Trickle-bed) (see Burghardt et al., 1995), m
μ	viscosity (dynamic), Pa s
ρ	density, kg/m ³
σ	surface tension N/m
ϕ_H	hydrogen flowrate, mol/m ² /s
Ψ	liquid slug length aspect ratio ($=L_{\text{slug}}/dh$) (typically: =3), dimensionless

Subscripts

cat	catalyst
<i>g</i>	gas
<i>gl</i>	gas–liquid
<i>gs</i>	gas–solid
<i>H</i>	hydrogen
<i>l</i>	liquid
<i>ls</i>	liquid–solid
<i>S</i>	styrene
Sulf	sulfur component (thiophene)
<i>b</i>	in liquid bulk (monolith model)
<i>c</i>	at catalyst
<i>d</i>	dynamic liquid phase (trickle bed model)
<i>cg</i>	at catalyst in contact with gas phase (trickle bed model)
<i>s</i>	stationary liquid phase (trickle bed model)
sat	saturated

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