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Bottom-mounted ATR probes: Pitfalls that arise from gravitational effects

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Abstract

For practical reasons, ATR-IR probes are usually mounted in the bottom of an autoclave, inside a small cavity. Using a transparent mock-up, we observed that it is very likely that catalyst particles settle inside this cavity, right above the crystal. The impeller speed needed to remove these deposited particles depends on the impeller dimensions and the density of the catalyst particles. Trends in this catalyst settling behaviour agreed with the Zwietering' correlation indicating poor mixing characteristics due to the presence of the cavity. The presence of a layer of catalyst particles on the crystal leads to overestimation of the observed reaction rates measured by ATR-IR. Several indicative experiments of the hydrogenation of naphthalene to decalin over Pd-based catalysts, involving step changes, showed dynamic responses and trends in observed reaction rates that can be used to reveal these effects in closed autoclaves. A simple model that assumes an ideally mixed bulk phase and a stagnant layer of catalyst particles in the cavity describes the observed phenomena well.

Keywords: ATR-FT-IR spectroscopy; Heterogeneous catalysis; Particle settling; Mass transfer; Hydrogenation; Naphthalene; Pd/$BaSO_4$; Pd/Al_2O_3

1. Introduction

The analysis of heterogeneous catalysts in the working state, i.e. *operando analysis* [1–3], has been a major focus of the catalysis community in recent years. More and more, we realize that the reaction conditions (temperature, partial pressure of reactants and products) have a major impact on the structure of the heterogeneous catalyst, and we need to study the catalyst while it is at work. Post-reaction analysis often provides misleading or at least insufficient information. Non-invasive analysis techniques such as Raman and infrared spectroscopy have been applied extensively in the analysis of heterogeneous catalysts 'at work' in gas phase processes. More recently, attenuated total reflection (ATR) infrared spectroscopy has been successfully applied in studying heterogeneous liquid phase processes [4], using real powder catalysts, even in photocatalytic applications [5,6]. Literature on ATR studies of heterogeneous liquid phase processes is mostly limited to atmospheric pressure conditions [7], and concerned with solid–liquid interactions [8]. On the other hand, many industrially relevant processes in the liquid phase involve elevated pressures of typically hydrogen or oxygen, and the roles of these gaseous molecules can only be analyzed if the pressure can be varied over a sufficient range. For such high pressures commercially available systems exist in which an ATR crystal (typically diamond) is located in the bottom of an autoclave. In such autoclaves, changes in the reaction mixture, rather than catalyst–reactant interactions, can be followed *in situ* at high temperatures and pressures [9].

In an earlier work [10] we have analyzed the use of bench-scale autoclaves when mass transfer similarity to industrial units is crucial. When the low mass transfer rates of these large reactors are implemented in bench-scale units, one has to run the stirrer just slightly faster than the critical stirrer speed at which gas is sucked in. In this mode of operation, taking samples for subsequent off-line analysis changes the liquid level in the reactor, which in turn alters the mass transfer performance significantly. Based on this finding, we always check the impact of liquid level variations by running several downscaled hydrogenation experiments without taking samples, using the

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Nomenclature

A_{cavity}	surface area of the cavity (m^2)
C_{bulk}	concentration of naphthalene in the bulk of the liquid ($\mathrm{mol\,l^{-1}}$)
C_{cavity}	concentration of naphthalene in the cavity ($\mathrm{mol\,l^{-1}}$)
C_{H2}	hydrogen concentration ($\mathrm{mol\,l^{-1}}$)
d_{I}	stirrer diameter (m)
d_{p}	particle diameter (m)
d_{T}	tank diameter (m)
g	gravitational constant ($\mathrm{m\,s^{-2}}$)
k_{mt}	mass transfer rate constant ($\mathrm{m\,s^{-1}}$)
k_{r}	reaction rate ($\mathrm{m^3\,mol^{-1}\,s^{-1}}$)
N_{m}	critical mixing rate required for particle suspension
V_{cavity}	volume of the cavity (m^3)
w	weight of solids in suspension, per weight of liquid, times 100
Greek symbols	
β_2	proportionality constant
μ_{L}	dynamic liquid viscosity (Pa s)
ρ_{L}	liquid density ($\mathrm{kg/m^3}$)
ρ_{p}	particle density ($\mathrm{kg/m^3}$)

hydrogen flow through the pressure controller to measure the conversion, and we compare these conversion levels with the experiments in which samples are taken for off-line analysis. On-line ATR allows selectivity and conversion to be measured without changing the liquid level in the reactor during an experiment, and in view of the above, in principle simplifies reliable kinetic evaluation. Unfortunately, complications still occur. These complications are the subject of this paper.

Here, particular attention will be given to the fact that the ATR crystal is subsided inside a small cavity in the bottom of the autoclave. Mounting the probe at the sidewall of the reactor would cause fewer problems, but in practice bottom mounting of the probes is more common. This probably stems from the fact that in single-phase homogeneous catalysis, the location of the probe is much less critical, and practical considerations in machining favour mounting the probe axisymmetrically in the bottom, while the heating mantle remains unpenetrated.

We will demonstrate some of the pitfalls that can arise from operating ATR-IR autoclaves in which the fluid and catalyst above the ATR crystal remains undisturbed at low stirrer speeds. Low stirring rates are usually applied to mimic industrial operations, to check the influence of mass transfer on selectivity and conversion or to prevent damage on fragile solid particles such as enzymes. Apart from gas induction, suspending catalyst is the most crucial phenomenon for the proper operation of bench-scale units. Significant misinterpretation of experimental data using ATR in autoclaves can occur if, because of the reduced exchange with the bulk liquid, most of the catalyst remains near the probe. This will be demonstrated in the present paper using naphthalene hydrogenation with Pd catalysts of varying density as an example; a reaction that is of potential interest in the framework of hydrogen storage in organic molecules [11,12].

2. Experimental

2.1. Cold flow experiments

The hydrodynamics and catalyst movement were investigated under non-reacting, ambient conditions in so-called cold flow experiments, using a transparent mock-up of the autoclave. The mock-up was geometrically identical to the high-pressure autoclave, incorporating a cavity of 10 mm in diameter and 3.5 mm deep, similar to the one present in the metal autoclave. The only difference is the internal diameter of 8 cm, compared to 7.5 cm in the autoclave. Hexane (95%, Acros organics) was used as a liquid to study settling behaviour of Al_2O_3 and $Pd/BaSO_4$ particles as a function of impeller speed. The viscosity (2.97×10^{-4} Pa s) and density (729 $\mathrm{kg/m^3}$) of *n*-hexane at room temperature are similar to those of the solvent *n*-decane at reaction conditions (viscosity 2.60×10^{-4} Pa s; density 713 $\mathrm{kg/m^3}$).

In particular, experiments were performed with catalyst amounts of 0.13 g and 1.3 g of Pd/Al_2O_3 and $Pd/BaSO_4$ suspended in 250 ml, corresponding to respectively 10% and 100% of the catalyst amounts used in experiments carried out in the autoclave. The stirring rate was varied from 0 to 1500 rpm. Photographs of the bottom of the mock-up were made during the experiments.

2.2. ATR-FT-IR set-up

Reactions were performed in a Premex Hastelloy C batch autoclave. The reactor volume is 500 ml (internal diameter 7.5 cm), the maximum allowable temperature is 190 °C and the maximum pressure is 80 bar. The maximum stirring rate is 1500 rpm, using a radial gas inducing impeller with a diameter of 5 cm. A schematic drawing of this autoclave set-up is given in Fig. 1.

The autoclave was modified with an ASI Applied Systems Dicomp (diamond-composite) ATR-FT-IR sentinel probe having nine internal reflections. The crystal was mounted in a cavity (10 mm in diameter and 3.5 mm deep) in the bottom of the autoclave.

Through a K7 conduit set-up, the probe was connected to a React-IR™ 1000 spectrophotometer, both were obtained from ASI Applied Systems, Millersville, MD. A liquid nitrogen cooled MCT (Mercury, Cadmium, Telluride) detector was used outside the spectrophotometer. React IR software (Version 2.21©) of ASI Applied Systems was used to process the gathered data.

2.3. Naphthalene hydrogenation experiments

Naphthalene hydrogenation reactions were carried out at 423 K and 50 bar of hydrogen (99.5%, Hoekloos). The reaction medium consisted of 5 mol% naphthalene (99+% gc, Acros) in

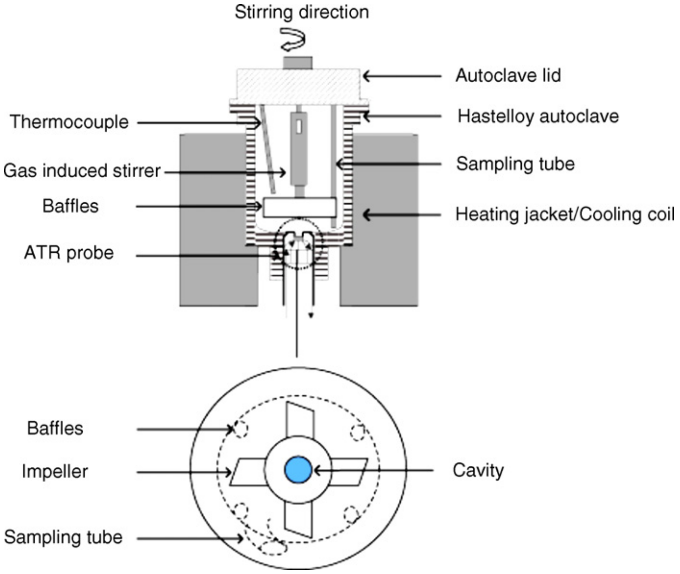

Fig. 1. Systematic drawing of the high-pressure autoclave set-up; side view and bottom view.

n-decane (94+% gc, Merck), with a total volume of 300 ml. Reactions were catalyzed by Pd supported on either Al_2O_3 (5 wt%, Sigma–Aldrich) or $BaSO_4$ (5 wt%, Sigma–Aldrich). Tetradecane (99%, Acros organics) was used as an internal standard. For all experiments, a palladium to naphthalene weight-ratio of 1:100 was used. In all experiments, the operation procedure was the same. The autoclave was first flushed with nitrogen and hydrogen was added once the temperature was constant at 423 K. During the experiments, the naphthalene concentration was measured with ATR-FT-IR and off-line GC. The GC used a CP-Sil8 CB column of 50 m, with an internal diameter of 0.25 mm, a film thickness of 0.12 μm and a Chrompak liquid sampler CP 9050.

Three experiments are reported in this work. The first experiment was performed with an impeller speed of 500 rpm and low-density Pd/Al_2O_3 catalyst particles ($\rho_P = 1.58 \times 10^3$ kg/m^3). In the second experiment, high-density Pd/$BaSO_4$ catalyst ($\rho_P = 2.27 \times 10^3$ kg/m^3) was used with an initial stirring rate of 400 rpm. After 37 min of reaction the stirring rate was increased to 1500 rpm. The third experiment was also catalyzed by Pd/$BaSO_4$ and was carried out at 500 rpm. Hydrogenation took place with an initial pressure of 50 bar and applying a step change to 1 bar after 64 min of reaction.

3. Results

3.1. Cold flow experiments

Cold flow experiments were performed with a low loading of high-density Pd/$BaSO_4$ catalyst, a high loading of high-density Pd/$BaSO_4$ catalyst, and high loading of low-density Pd/Al_2O_3 catalyst, respectively.

Fig. 2 shows the results for four different stirrer speeds, and a suspension of 0.12 g of Pd/$BaSO_4$. The impeller speed at which gas starts to be induced was 350 rpm, similar to the speed required to initiate suspension of the particles out of the cavity. The critical impeller speed for complete suspension is about 600 rpm. As can be seen in Fig. 2(d), the catalyst present at the rim of the bottom was hardest to suspend.

Similar experiments were performed using 1.3 g of Pd/$BaSO_4$ catalyst, which equals the catalyst concentrations used in reactive experiments in the autoclave. The impeller speed at which gas induction starts to take place does not change noticeably from the value of 350 rpm that is obtained at lower loading. In contrast to the experiments at low loading, the critical impeller speed for complete suspension increases from 600 to 900 rpm. Fig. 3 shows the behaviour of the catalyst particles at 500 rpm, which is the stirrer speed that we used for several reactive experiments. A large amount of catalyst remains deposited right above the cavity. The catalyst on the bottom hardly exchanges with the suspended catalyst and shows only a calm circulating motion; for all practical purposes this catalyst can be regarded as stagnant.

Finally, a similar set of experiments was performed with 1.3 g of the lighter Pd/Al_2O_3 particles. For these catalysts, only

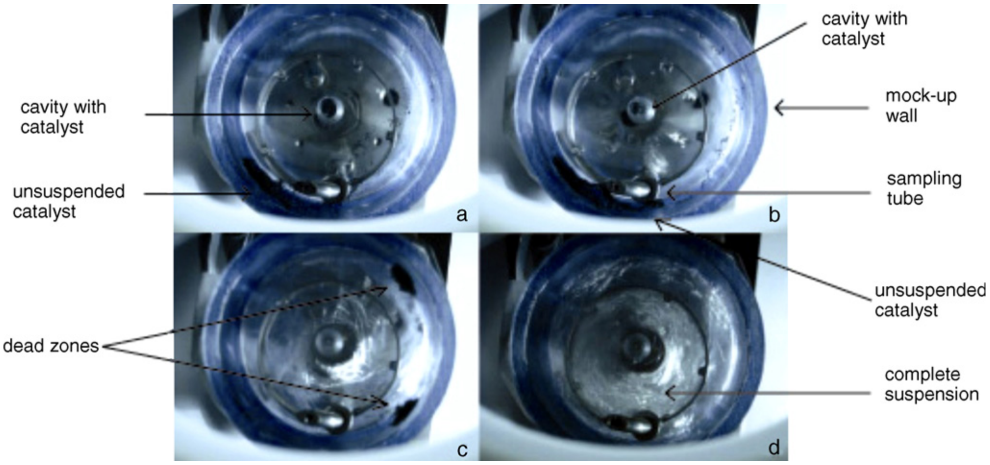

Fig. 2. Bottom view of the transparent mock-up of the autoclave. Effect of impeller speed on particle settling of 0.12 g of dark-coloured Pd/$BaSO_4$ catalyst: (a) at 300 rpm, much catalyst remains stationary in the cavity; (b) at 350 rpm, some catalyst remains in the cavity; (c) at 500 rpm no more stationary catalyst is present in the cavity; (d) at 1000 rpm all catalyst is suspended.

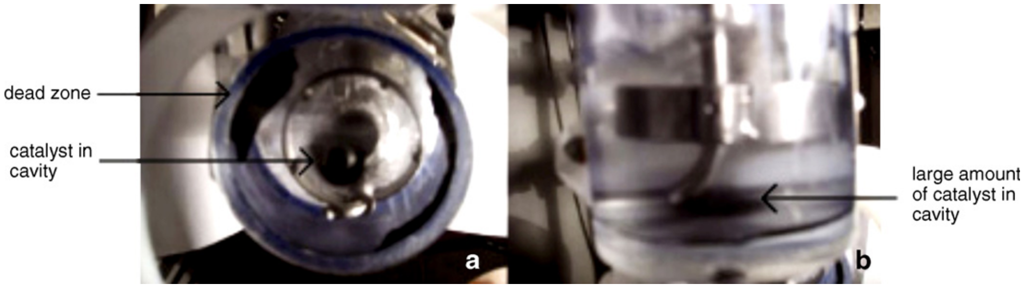

Fig. 3. Particle settling behaviour of 1.3 g of Pd/$BaSO_4$ at an impeller speed of 500 rpm: (a) bottom view; (b) side view.

500 rpm was needed to fully suspend the catalyst, compared to 900 rpm for the denser Pd/$BaSO_4$ catalyst.

3.2. Naphthalene hydrogenation

For all naphthalene hydrogenation reactions, IR absorbance signatures of naphthalene (780 cm^{-1}) and tetralin (740 cm^{-1}) can be clearly seen; see Fig. 4a. Decalin peaks are more difficult to find in the spectra, because these overlap with the solvent peaks.

As mentioned above, particles of Pd/Al_2O_3 are completely suspended at a stirring rate of 500 rpm. We performed a naphthalene hydrogenation run using this Pd/Al_2O_3 catalyst at 500 rpm under a pressure of 50 bar and 150 °C. Fig. 4b shows the concentration profiles of naphthalene as measured by online IR and off-line GC. Clearly, the IR data are in good agreement with the GC data, as has been observed previously [13].

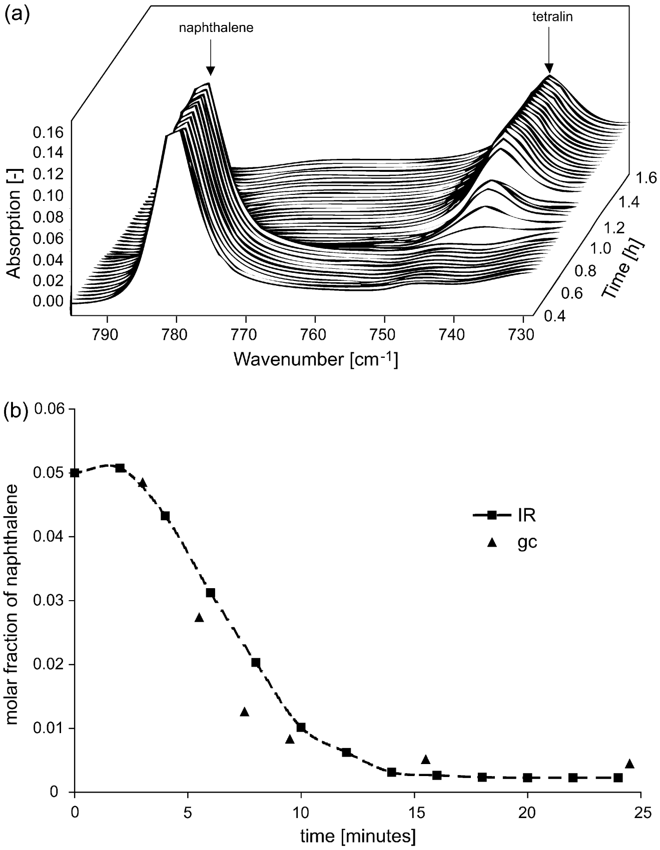

Fig. 4. The concentration of naphthalene as measured by IR and gc during hydrogenation at 150 °C and 500 rpm, catalyzed by Pd/Al_2O_3: (a) real-time waterfall plot as obtained by IR; (b) corresponding naphthalene concentrations.

A second reaction of naphthalene was carried out at the same conditions but using the faster settling Pd/$BaSO_4$ catalyst. We started this experiment with a low stirrer speed, of 500 rpm, so a large amount of catalyst remains stagnant on top of the cavity. Fig. 5 shows the concentration of naphthalene as measured with the IR probe. Under these conditions, it appears as if the reaction proceeds with first-order behaviour after an induction time of about 10 min. After 38 min, we increased the stirrer speed to 1500 rpm. Immediately, the concentration as measured by IR jumps, within a minute, to 85% of the initial value and then slowly decreases as the reaction proceeds.

In a second experiment with Pd/$BaSO_4$ catalyst, using a low stirring rate (Fig. 6), a step-change in hydrogen pressure was implied from 50 to 1 bar. Before the release of pressure, the measured concentration agrees with the previous experiment, although the reaction rate appears to be slightly higher. After the release of pressure, the measured concentration increases to 85% of the initial concentration, similar to the experiment previously described, except that the concentration increased much more slowly: it took about 80 min to reach 85%.

4. Discussion

4.1. Cold flow experiments

The cold flow experiments demonstrated that the cavity in which the ATR probe is located remains filled with catalyst

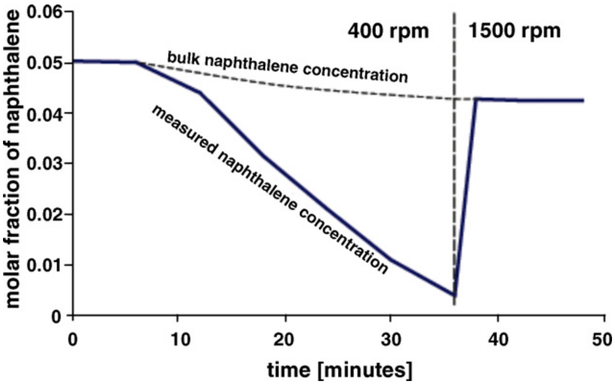

Fig. 5. Effect of a sudden increase in impeller speed from 400 to 1500 rpm on the naphthalene concentrations as measured by ATR-FT-IR. Hydrogenation of naphthalene (50 bar H_2, 150 °C) was performed using fast-settling Pd/$BaSO_4$ catalyst particles.

particles below certain stirrer speeds. This problem is more severe when large amounts of fast-settling catalysts are used. Many relations have been published [14–16] for the critical impeller speed required for complete suspension of the particles. The most widely used relation is described by Zwietering [14]:

$$N_m = \frac{\beta_2 d_P^{0.2} \mu_L^{0.1} g^{0.45} (\rho_p - \rho_L)^{0.45} w'^{0.13}}{\rho_L^{0.55} d_l^{0.85}} \tag{1}$$

Eq. (1) is primarily a balance of fluid inertia ($\sim\rho_L \pi N^2 d_I^2$) and particle buoyancy ($\sim(\rho_p - \rho_L) g d_P$), with minor other contributions based on experimental data. Eq. (1) identifies the most relevant parameters: the density and size of the particles, and to a lesser extent the catalyst loading. The experiments performed in this paper, albeit limited in number, confirm the parameter dependencies of Eq (1). In Eq. (1), the proportionality constant β_2 is a constant dependent on the autoclave and impeller design. For a standard Rushton autoclave, the proportionality constant has been correlated as [17]:

$$\beta_2 = 2\left(\frac{d_T}{d_I}\right)^{1.33} \tag{2}$$

The proportionality constant β_2 of the autoclave used in this work was found to be 5.5, which is about two times higher than for a standard Rushton autoclave of the same dimensions. This indicates that our autoclave design is not optimal for catalyst suspension, which is partly caused by the cavity in the bottom of the autoclave. This also constitutes a warning against the use of correlations for flat-bottomed vessels. At the location of probes and appendages, the local geometry and flow conditions are often too far from the idealized flat-bottom case, so unadjusted use of correlations give false results.

We observed a 50% increase in the critical impeller speed when using 10 times more catalyst, and Eq. (1) predicts 37%. The difference is probably related to the use of a gas inducing impeller. At higher impeller speeds, more gas is induced and the amount of energy dissipated by the impeller goes down [10].

Correlations such as Eq. (1) are valuable in estimating the required stirrer speed, but they should be used with care. Apart from the mock-up that closely mimics our autoclave, we have also tried several mock-ups of slightly different geometry. Especially a rounded bottom reduced the required stirrer speed for catalyst suspension. Suspension experiments are relatively easy to perform, and visual observation is preferred, using the exact catalyst and exact geometry that are used in the reactions.

4.2. Naphthalene hydrogenation

The first experiment (Fig. 4) was conducted under conditions where all the catalyst was fully suspended. The data from off-line GC analysis and the IR-probe agreed. No surprises were encountered, which agrees with the observations from the cold flow experiments.

In the second experiment, presented in Fig. 5, the only change with respect to the previous experiment was the use of a more dense catalyst. The cold flow experiments indicated that these dense Pd/$BaSO_4$ particles accumulate in the cavity. It is instructive to make a balance over this stagnant amount of catalyst. In the following estimate we assume that the cavity is filled with catalyst and that the fluid flow above the cavity sweeps the catalyst away. As the cavity is much wider than it is deep, the characteristic diffusional distance is given by the depth of cavity (that is, V_{cavity}/A_{cavity}). If we assume a pseudo-steady-state concentration of reactants in the cavity, we can balance the reaction rate $k_r C_{H2} C_{cavity} V_{cavity}$ with the mass transfer to the cavity $k_{mt} A_{cavity}(C_{bulk} - C_{cavity})$, where k_r is a first order rate constant, k_{mt} a mass transfer coefficient, C_{bulk} the naphthalene concentration in the well-mixed bulk above the cavity, C_{cavity} the naphthalene concentration in the cavity, and C_{H2} is the hydrogen concentration in the cavity. We can rearrange this to obtain:

$$\frac{C_{cavity}}{C_{bulk}} = \frac{k_{mt} A_{cavity}}{k_r C_{H2} C_{cavity} V_{cavity} + k_{mt} A_{cavity}} \tag{3}$$

Only the local concentration of naphthalene, C_{cavity}, is measured with ATR-IR. Eq. (3) predicts the behaviour we have observed by applying a step change in the stirring rate (Fig. 5) or the hydrogen pressure (Fig. 6).

Because the mass transfer is slow with respect to the reaction, the concentration inside the cavity will be lower than the bulk concentration. So, the fast decay of naphthalene in the first 30 min of the experiment in Fig. 6 just shows the fast depletion of naphthalene in the cavity. The depleted naphthalene apparently cannot be replenished by mass transfer of naphthalene from the bulk. In order to prevent drawing false conclusions from experiments carried out under unfavourable mixing conditions, measurements should take place at multiple regions of the autoclave. For such purpose, several analytical techniques can be combined.

The induction period is a measure for the time it takes for the hydrogen to diffuse into the cavity. The characteristic length of the cavity is about $L = 3$ mm, and the diffusion coefficient of hydrogen in *n*-decane at 150 °C is 3.1×10^{-8} m^2/s. A rough calculation can be made using the penetration time as

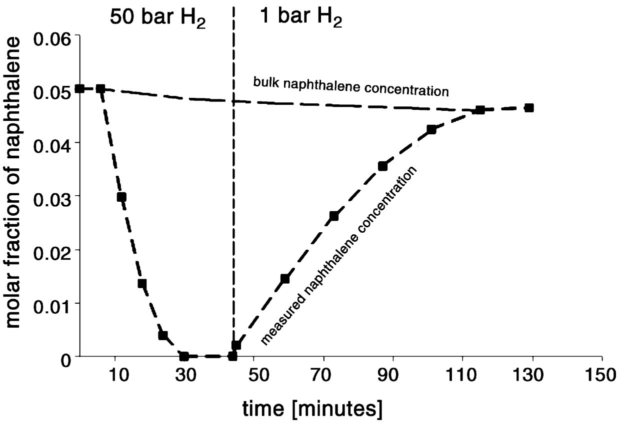

Fig. 6. Effect of an instantaneous decrease in hydrogen pressure from 50 to 1 bar. Hydrogenation of naphthalene (500 rpm, 150 °C) was performed using fast-settling Pd/$BaSO_4$ catalyst particles.

calculated by

$$t = \frac{L^2}{D_{H2}} \qquad (4)$$

The penetration time thus calculated is 5 min, which agrees nicely with the observed induction time.

In Fig. 5, the increase in stirring rate suspended the catalyst particles and mixed the liquid phase. The naphthalene concentration as measured by IR consecutive to the increase in stirring rate is equal to the average concentration of naphthalene in the autoclave.

In Fig. 6, the decrease of the hydrogen pressure led to a strong decrease in the reaction rate. Naphthalene can now diffuse through the catalyst layer without reacting away so fast, and the concentration as measured by IR increases. The chemical equilibrium at these conditions is still far towards the hydrogenated product.

Again, we estimate the time it takes for the concentration to reach the new level using Eq. (4), but now with the diffusion coefficient of naphthalene, which is 10 times lower than that of hydrogen (3.7×10^{-9} m^2/s). As a result, the estimated time for naphthalene to penetrate to the probe is 55 min, which agrees sufficiently well with the experimental value of 80 min.

Fig. 7 gives a possible development of the reaction rate measured by ATR-IR. At the lowest stirring rates, mass transfer of hydrogen is limiting. At slightly higher stirring rates, gas induction starts to occur, but the stagnant layer of particles remains present. At such conditions, the stirring rate will not significantly influence the reaction rate measured by ATR-IR and the false conclusion may be drawn that the system is well mixed. Also, the ATR-IR measurements give a false impression of a fast reaction, whereas the GC measurements do reflect the slow reaction of the bulk liquid. Above a critical stirring rate for catalyst suspension, the observed rate of reaction as measured by ATR-IR collapses to the value measured by GC. From this point on, the concentrations measured by ATR-IR are a good measure for the bulk concentrations. Increasing the stirring rate further improves the mass transfer rates until all these mass transfer steps are not limiting anymore and the catalyst performs at its maximum effectiveness.

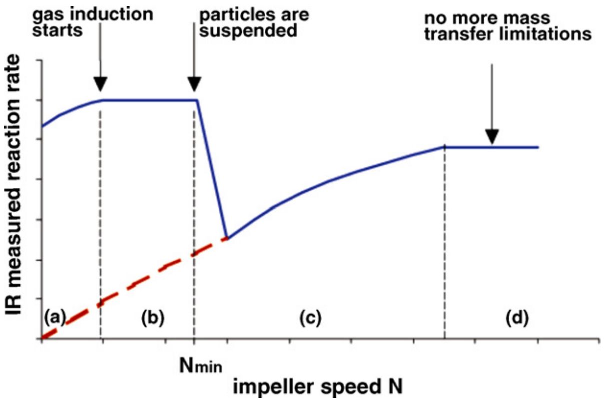

Fig. 7. Possible development of the measured reaction rate under changes in the impeller speed. The dotted line indicates gc measurements and the solid line indicates ATR measurements.

In short, the IR measurements can be explained by using the cold flow observations and by considering a simple balance for the region above the IR-probe.

5. Conclusions

In this work the suspension of catalysts in an ATR-IR autoclave has been evaluated. The ATR crystal is located in a cavity in the bottom of the autoclave, which affects the suspension behaviour of catalyst particles. Several conclusions can be drawn.

Trends in suspension agree with the classical correlation as found by Zwietering [14]. However, the proportionality constant in the correlation for the minimal stirrer speed was found to be 5.5, which is about two times higher than for a normal rushton autoclave. This high value is a result of the cavity above the ATR probe, where catalyst settling occurs.

At low impeller speeds a layer of immobile catalyst particles is present in the cavity leading to an overestimation of the reaction rate as determined by ATR spectroscopy. At such conditions the reaction rate is nearly independent on the impeller speed, which might lead to the wrong impression of having a well-mixed system.

The observed phenomena at low impeller speeds could be explained by a model that assumes an ideally mixed bulk phase, and a stagnant layer of catalyst particles in the cavity.

Interpretation of IR spectra after applying a step change in pressure or stirring rate shows the presence or absence of a stagnant catalyst layer above the crystal.

Based on the findings described here, it is recommended to carry out cold flow experiments in a mock-up very similar in shape to the autoclave and study catalyst settling behaviour before commencing with any reactions.

In case reactions have to be carried out under non-ideal mixing conditions, concentrations should be measured at more than one height in the reactor. This can be achieved by combining several analytical techniques.

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