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Aqueous biphasic catalysis: Where the reaction takes place

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Abstract

Aqueous biphasic catalytical processes are still in the infancy of their significance: their decisive advantage (the easy separability of catalyst and product) will grow in importance even for reactions other than the economic and industrially proven hydroformylation. Despite relevance to industry, some basic facts about them remain unclear, such as the question as to where the reaction takes place. The location of the biphasic reaction is contested: is it the bulk of the aqueous catalyst solution or the interfacial layer aqueous/organic liquid? For RCH/RP's oxo process this question can be decided by methods of reaction modeling and the comparison with experimentally proven facts, thus leading to scale-up rules and appropriate kinetic models as a basis for the optimal reactor design. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Biphasic catalysis in its particularly attractive aqueous variant has been known for around 20 years since initial postulation by Manassen [1]. The sequence in which it was developed is unusual: initial experimental work by an industrial chemist (E.G. Kuntz, [2], then of Rhône-Poulenc), industrial practice since 1984 after the pioneering development work at Ruhrchemie AG on the 'Ruhrchemie/ Rhône-Poulenc (RCH/RP) process' [3] and only then, for about the last 8 years, more detailed scientific study. The papers in this special issue confirm this unusual sequence-economic utilization well before scientific investigation very clearly. The topics of the following papers illustrate yet again what a narrow path the successful propylene hydroformylation cut through the jungle of totally unknown fundamentals in biphasic catalysis during the industrial development of the process between 1982 and 1984. The topic of this special issue results from the papers presented at the Symposium on Phase-Separable Homogeneous Catalysis in Las Vegas, NV and will occupy a fair number of researchers in the future.

In this paper, we report on further advances in homogeneously catalyzed propylene hydroformylation for the preparation of *n*-butyraldehyde (Fig. 1) using aqueous, ligand-modified rhodium (Fig. 2) complex solutions with a special focus on experiments that confirm the reaction to take place in the interphase region and not the bulk aqueous phase (which has been suspected earlier but not using the most appropriate arguments [4]). The RCH/RP process is outlined schematically in Fig. 3.

Although the industrial oxo synthesis uses olefins with up to 16 carbon atoms, the aqueous, biphasic

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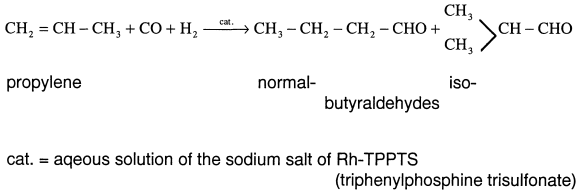


$$CH_2=CH-CH_3+CO+H_2 \xrightarrow{cat.} CH_3-CH_2-CH_2-CHO + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-CHO$$

Fig. 1. Hydroformylation (oxo synthesis, Roelen reaction) of propylene.

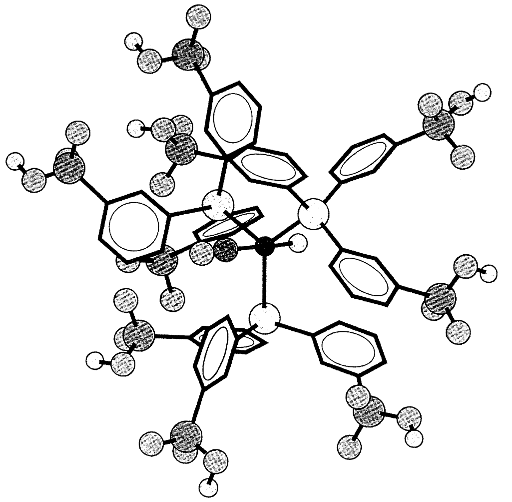


Fig. 2. [HRh(CO)(TPPTS)3], the catalyst of the RCRP process

variant has so far only been applied to propylene and butylenes.

Due to the possibility of entanglement, including linguistic confusion, it should be made clear that the biphasic hydroformylation catalysis is *homogeneous*. This is easily confirmed since *all* criteria of a homogeneously catalyzed reaction are fulfilled. Specifically the catalysts are, inter alia, molecularly dispersed, unequivocally characterized both chemically and spectroscopically, pass through a detectable catalyst cycle, and permit the unequivocal determination of reaction kinetics [5].

Nevertheless, the catalyst is *heterogeneous* in relation to the reactants (an aqueous catalyst solution is charged with liquid or gaseous reactants), the reactants are then heterogeneous, namely gaseous and liquid, with respect to one another, and the reaction product is also in a different liquid phase – i.e. *heterogeneous* – with respect to the catalyst. In reality, therefore, this is a triphasic reaction, which is only tacitly referred to as 'biphasic' because gas phases are not counted separately in catalytic reactions.

In this type of biphasic reaction, the site of the reaction is disputed: is it the bulk of the liquid or the phase interface? In a reaction in the bulk of the liquid, the liquid and gaseous reactants would first have to be dissolved in the aqueous catalyst solution at relatively high mass transfer velocities before the chemical reaction commences, at a comparatively low reaction rate. The reaction rate is, therefore, determined by the concentrations of the gaseous reactants in the *liquid* phase. According to the phase interface theory, the current concentrations in the *gas* phase should be the crucial factors in its kinetic model. Evidence of the validity of one of the two theories has so far mainly been provided indirectly and through postulated effects of the reaction-accelerating engineering measures or additives. For example, it has been suggested that the positive effects of co-solvents and other solubility promoters (for example lower alcohols) indicate that the bulk of the liquid is the reaction site [6]. The decrease in the solubility of the starting olefins for the hydroformylation and the aldehydes formed from them in water with increasing number of carbon atoms is illustrated in Fig. 4 and the decrease in reactivity of the starting olefins which occurs in parallel are also called on to confirm the bulk of the liquid as the reaction site.

It is evident that this decrease in the solubility of higher olefins offers poor prospects for their use (and consequently their reactivity) in the RCH/RP process, if the reaction site is taken to be the bulk of the liquid. However, this overlooks the fact that higher olefins also generally react more slowly under otherwise identical conditions in classical *monophasic* hydroformylation. By contrast, addition of surfactants or other surface- or micelle-active compounds in order to accelerate the reaction or measures which promote mixing apparently indicate that the interfacial layer is the site of the reaction [7].

In this paper, we report on attempts to find evidence for the site of the reaction in biphasic hydroformylation, or more precisely in the RCH/RP process using propylene. To do this, relatively simple autoclave experiments were carried out at various pressures, temperatures, stirrer speeds, etc., and the consistent results discussed.

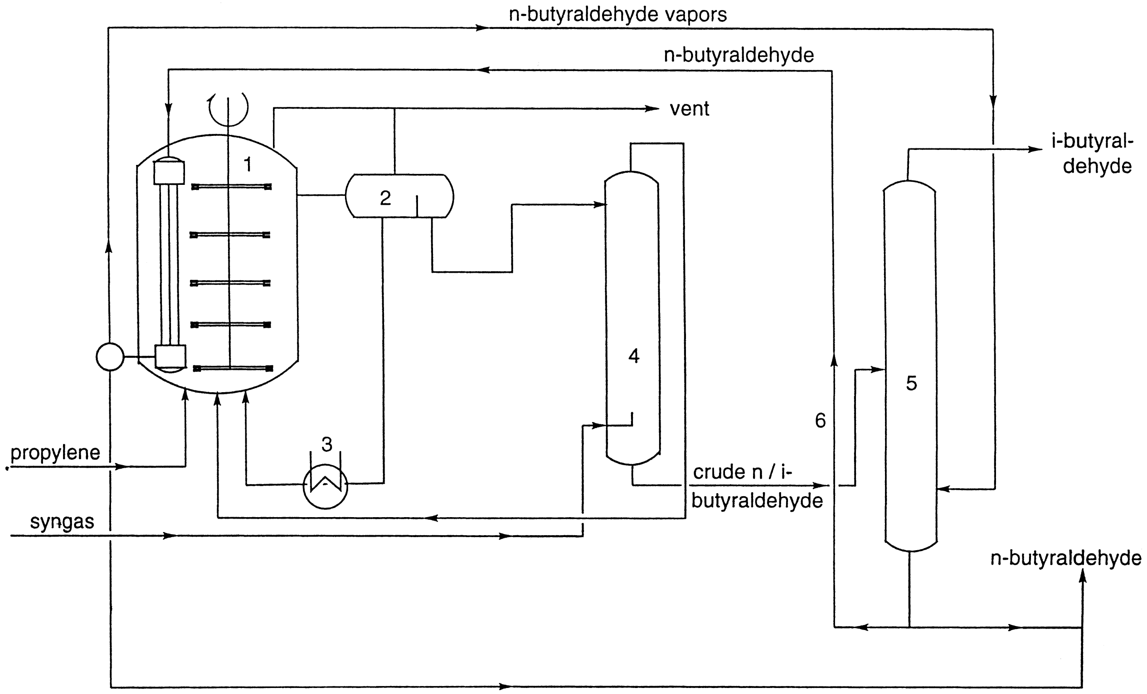


Fig. 3. The Ruhrchemie/RP process; (1): Reactor; (2): Decanter; (3): Heat exchanger; (4): Stripping column; (5): Distillation (*n*/iso column) (6): Recycle of the coolant *n*- butyraldehyde.

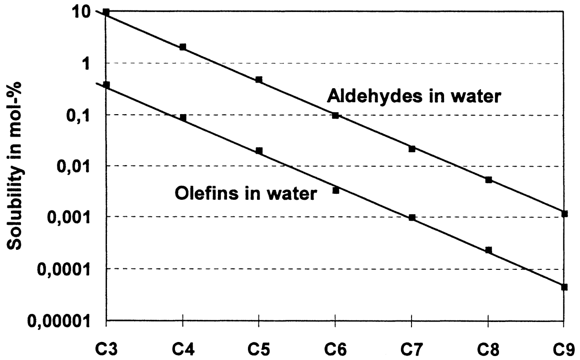


Fig. 4. Solubility of olefins and aldehydes in water.

2. Results and discussion

The experimental work was based on the batch calorimetric experiments at different stirrer speeds, temperatures, and concentrations, using an autoclave with a 4-tube hollow stirrer and catalyst solutions from the large-scale plants at Oberhausen. The gas/liquid mass transfer coefficient (k_La) and the gas/liquid interfacial area (a) were already known from model studies using an air/water model mixture. The tank (batch) stirred reactor and the stirrer behavior, which is an important parameter in simulating the true conditions in the large-scale industrial process, is illustrated in Fig. 5.

The gassing experiments (Fig. 5) show, as expected, a significant increase of the liquid level the ebullating bed through an increase in the gas (bubble) content of the liquid with increasing stirrer speed. This growth of

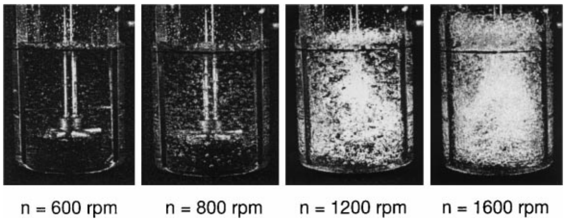

n = 600 rpm n = 800 rpm n = 1200 rpm n = 1600 rpm

Fig. 5. Photographs of the glass autoclave used for the batch calorimetric experiments at different stirring rates to demonstrate the gas/liquid mixing.

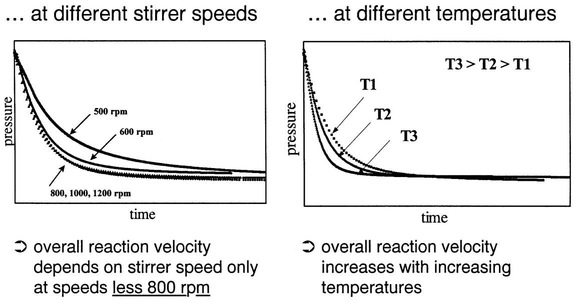


Fig. 6. Pressure uptake in the batch hydroformylation of propylene as a function of stirrer speed and temperature.

the available phase interface results in an increase in the reaction rate as shown in Fig. 6.

The experiments at various temperatures show the expected increase in the overall reaction rate with reaction temperature. According to the experiments with varying stirrer speed, the overall reaction rate is independent of the stirrer speed at above 800 rpm. There should therefore be no limit on mass transport at speeds above 800 rpm (or on the other hand coalescence effects prevent the increase of more interfacial area). The experimental results and the results from model experiments mentioned before allow kinetic equations of the type exemplified in Fig. 7 and Fig. 8 to be given for the two models postulated, namely a reaction in the bulk water phase (model A) or a reaction at the phase interface (model B).

The progress of reactions which take place in different phases as in the gas/liquid system here and their overall reaction rate are determined by the actual reaction rate and by mass the transport processes or the ratio between the two. The fundamentals of such reactions are shown in Fig. 9.

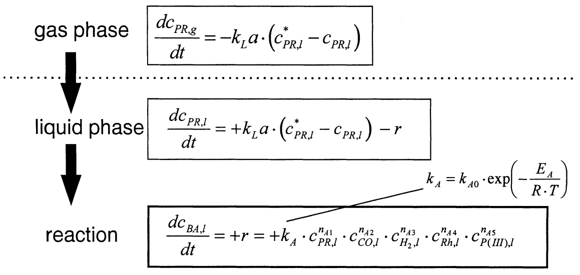


Fig. 7. Kinetic equations for the reaction model A in which the reaction takes place in the bulk of the liquid phase.

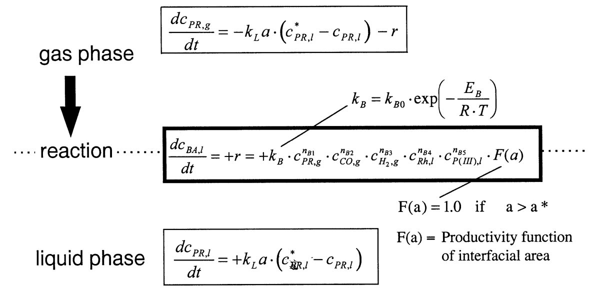


Fig. 8. Kinetic equations for the reaction model B in which the reaction takes place in the interphase region.

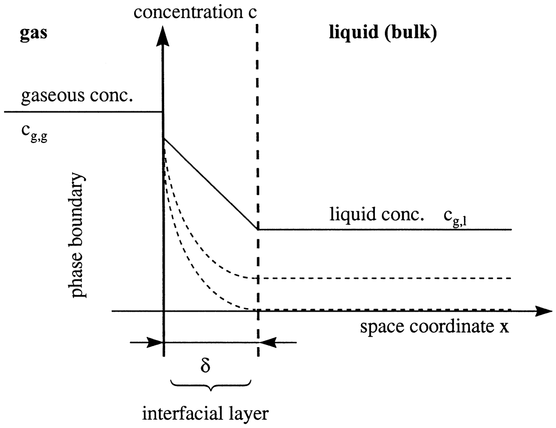
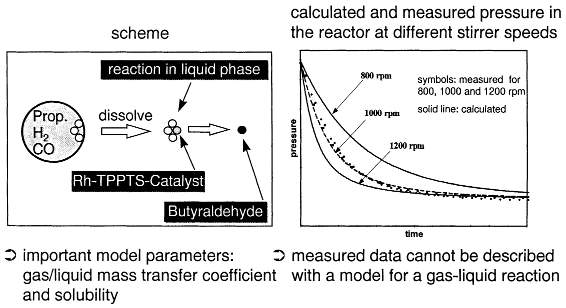


Fig. 9. Basic considerations for reactions in the gaseous/liquid phase.

Consequently, in reactions which occur in the bulk of the liquid phase, the concentration of the gaseous component (e.g. CO) in the gas phase ($c_{g,g}$) within an interfacial layer with an assumed thickness, δ is reduced merely to the concentration $c_{g,l}$ (the concentration of the gaseous component in the liquid phase) by physical diffusion processes. At a low reaction rate relative to these mass transport processes the value $c_{g,l}$, will apply to the entire liquid phase, so that the reaction rate is proportional to the concentration $c_{g,l}$ in the liquid phase and also to the volume of the liquid phase: the gaseous reactants have already become uniformly distributed in the liquid phase owing to the rapid mass transport somewhat before the actual, and slower, chemical reaction commences.

This model A contrasts with the idea of a relatively rapid chemical reaction as opposed to mass transport. The fact that the gaseous reactants react very quickly


scheme

calculated and measured pressure in the reactor at different stirrer speeds

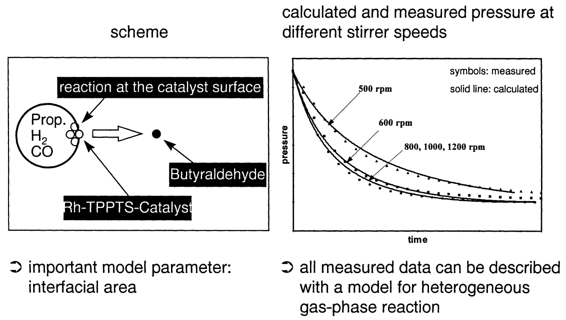
➲ important model parameters: gas/liquid mass transfer coefficient and solubility

➲ measured data cannot be described with a model for a gas-liquid reaction

Fig. 10. Comparison of the calculated pressures (solid lines) in the batch reactor under model A, reaction in the bulk of the liquid phase vs. the experimental pressures (data points).

means that, in practice, the reaction takes place at the phase boundary or in an interfacial layer with a relatively small thickness, δ. This is model B assuming a reaction site at the phase interface (boundary). A fit of the experimental data to the predictions of models A and B are presented in Figs. 10 and 11, respectively.

The principle of model A and the diffusion from the gas phase into the liquid phase which precedes the chemical reaction is shown in the left-hand part of Fig. 10. Calculated and experimental pressure/time curves for three experiments at different stirrer speeds are shown on the right. The continuous lines show the *calculated* values for the bulk model, and the circles, squares and crosses show the effective *measured values*. It is clear that the bulk model does not describe reality: the bulk of the liquid is obviously *not* the site of the reaction. On the other hand model B (Fig. 11) proves better coincidence.

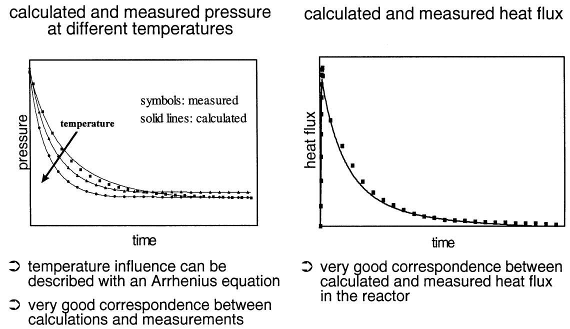

scheme

calculated and measured pressure at different stirrer speeds

➲ important model parameter: interfacial area

➲ all measured data can be described with a model for heterogeneous gas-phase reaction

Fig. 11. Comparison of the calculated pressures (solid lines) in the batch reactor under model B, reaction at the interfacial boundary vs. the experimental.


calculated and measured pressure at different temperatures

calculated and measured heat flux

➲ temperature influence can be described with an Arrhenius equation

➲ very good correspondence between calculations and measurements

➲ very good correspondence between calculated and measured heat flux in the reactor

Fig. 12. Simulated and experimental pressure change as a function of temperature and calculated and measured heat fluxes in model B.

Again the principle and the site of the reaction in model B directly at the phase boundary is shown in the left-hand part of Fig. 11. The calculated and measured pressure/time curves are shown on the right. These coincide in the extended stirrer speed range from 500–1200 rpm. This means that a model with the phase interface as the reaction site can be modeled well and is therefore more probable.

The fact that the change in pressure and heat flux as a function of time can also be described well and thus modeled by assuming model B is shown in Fig. 12 and supports model B. Consequently, it is clearly shown that any modeling based on the idea of a bulk reaction site provides unsatisfactory results. Only the assumption of a reaction at the phase interface provides results which can be correlated with all the experiments that have been carried out.

Consideration of the information in Fig. 9 shows that model B can be refined by varying the thickness, δ of the interfacial layer and consequently the ratio between mass transport and chemical reaction rate. In order to estimate the effect of this, a series of three batch hydroformylation experiments starting with 700, 500 and 350 ml of an aqueous catalyst solution (Rh-TPPTS) was carried out in a 2 l autoclave. The catalyst solution was heated to the reaction temperature, the autoclaves were then charged to 51 bar (728 pounds per square inch) with mixtures of CO, H_2 and propylene gases in the ratio 18:18:15, and the reaction was started by switching on the stirrer. Measurement of the change in pressure over time allowed the material flow in the three experiments to be determined. The results of these experiments are

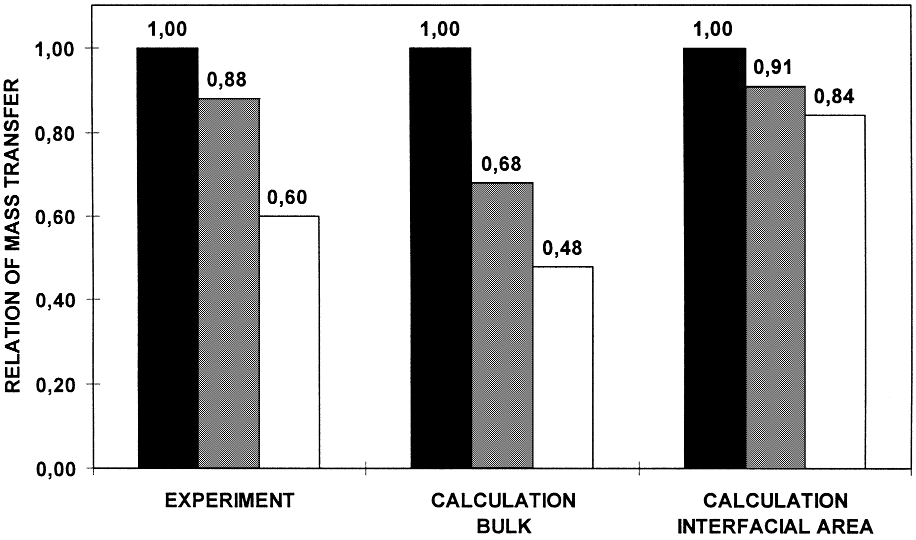


Fig. 13. Comparison of the experimental material flow ratios with the values calculated under models A and B.

presented in Fig. 13 along with the corresponding calculated values from models A and B.

The mass flow in the three experiments were in the ratio 1:0.88: 0.60. This result is not as expected taking into account the experimental conditions (free gas volume of the autoclaves under the given pressure, so different gas amounts, etc) and assuming a reaction in the bulk of the liquid, in which material flows in the ratio 1:0.68:0.48 – i.e. in the ratio of the corrected reaction volumes would have to arise. This is a further indication that the site of the propylene hydroformylation reaction in the aqueous biphasic variant cannot be the bulk of the liquid. Neither, however, does the assumption of a rapid reaction directly at the phase boundary third column in Fig. 13 result in agreement of the expected ratio 1:0.91:0.84 with the experimental results. This in turn leads to the conclusion that although the site of the reaction can be described by assuming a reaction in the interfacial layer, the unknown values in the Fick's Second Law (layer thickness δ and diffusion coefficient) must also be determined. We are currently refining the reaction model in order to improve the agreement between the model and the experimental results. The resultant model C will then allow further process- and reaction-related conclusions to be drawn. The results presented can be summarized as follows:

- Simple batch experiments together with reaction modeling were successful in locating the site of reaction for biphasic hydroformalation of propylene.
- The conversion is best described as a reaction in the liquid boundary layer at the gas/liquid interface and not as a reaction that occurs in the bulk of the liquid. Further modeling is required to refine the model details to provide parameters such as boundary layer thickness, δ.
- Preliminary scale-up rules for the process and kinetc models could be developed and used for the optimization of large scale production reactors.
- These knowledge will be transferred to the hydroformylation of higher olefins, such as octenes.

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