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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 photo-catalytic 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