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Design and operational limits of an ATR-FTIR spectroscopic microreactor for investigating reactions at liquid–solid interface

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HIGHLIGHTS

- An attenuated total reflection microfluidic cell was designed.
- Optimization of the inner flow was obtained by 3D numerical simulations.
- Transport of the reactant is characterized by convection and diffusion.
- Criteria to operate under chemical control are presented.
- CO adsorption in aqueous phase on platinum thin film is studied.

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ABSTRACT

This work presents the design and characterization of an optimized attenuated total reflection (ATR) microfluidic cell to assess intrinsic kinetic parameters of reactions at the liquid/solid interface under chemical control. A theoretical and computational investigation of convection, diffusion, and adsorption is presented. Transport dynamics in transient-flow experiments is characterized by a convective and diffusive mass transport of the solution species to the surface of the ATR crystal. Criteria to determine the mass transport limitations of the adsorption process are presented as a function of the Damköhler and Biot numbers. The CO adsorption on a thin film of platinum is studied in order to validate the model.

1. Introduction

For a rational design and optimization of new efficient catalytic systems, it is crucial to understand reaction mechanisms under reaction conditions, that is, identifying and monitoring chemical species involved in the reactions and finding relationships between structure and reactivity. To this end, significant advances have been done in the *in situ* investigation of catalysts under real conditions of operation, e.g. *operando* spectroscopies [1,2].

In order to correlate chemical reactive surface species with the observed reactivity (reaction rate, apparent activation energy), the spectroscopic cell must perform as an actual catalytic reactor. In a recent review of this topic, Meunier [2] point out that spectroscopic cells are typically not ideal catalytic reactors, since a compromise must be found between (i) allowing the electromagnetic wave to probe the catalyst and (ii) keeping the bed geometry and temperature/flow control appropriate. Thus, most of the *operando* reactors have been developed for studies of reaction in the gas(reactant)/solid(catalyst) interface. For instance, several cells in diffuse reflectance infrared spectroscopy (DRIFT) [3,4], Raman [5] and X-ray absorption spectroscopies (XAS) [6] have shown to behave as plug-flow microreactors. Conversely, less developed are the spectroscopic reactors to investigate heterogeneously catalyzed reaction in liquid phase, this is probably due to the fact that all problems listed before are augmented in the condensed phase.

Attenuated total reflection (ATR) infrared (IR) spectroscopy is an appropriate tool for the investigation of reaction pathways in liquid(reactive)/solid(catalyst) systems, because it provides the detection of species adsorbed on a catalyst under reaction conditions [7]. Catalysts are usually deposited on the internal reflection elements (IRE) as films (e.g. metal film) or as layers of powders, and they are exposed to the liquid phase reactants. Usually, the presence of strongly absorbent condensate phase (solvents and

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reactants), spectator species and/or the catalyst itself can make very difficult or preclude both the identification and tracking of the true active species, that is, the reaction intermediates. Then, transient experiments are widely applied in the analysis of reaction intermediates by perturbing a catalytic system working under steady state conditions (ss). Particularly, modulation excitation spectroscopy (MES) with phase sensitive detection (PSD) has proved to be an adequate methodology to study reactions in liquid/solid interfaces [7–10].

However, in most reported studies, an ATR cell is used as a qualitative technique to track surface intermediate species [7], and in some cases the measurement of kinetic data do not consider the mass-transport problems that are likely involved [11]. Therefore, to obtain quantitative information, that is, determining intrinsic reaction rates, the chemical engineering aspects of an ATR flow-through cell must be developed. Thus, to correctly extract the intrinsic kinetics information of chemical steps such as adsorption or surface reaction, mass transport in the ATR cell has to be considered. This point becomes even more important when multiple internal reflection elements (IRE) with high geometrical surface area are used in the ATR experiments in order to improve the signal-to-noise ratio. In this case the concentration may vary significantly not only with time but also in space. For instance, Baiker and co-workers [12] showed that, given the fluid dynamic characteristics of flow-through ATR cells, the mass transport phenomena are governed by a convection–diffusion mechanism. Later, Bieri and Bürgui [13] employed this model to calculated relative adsorption and desorption rates of proline on self-assembled monolayers of L-glutathione on gold by MES-ATR. Nevertheless to our knowledge no systematic and quantitative characterization of the impact of mass-transfer limitation to perform investigation in an ATR cell under kinetic control has been reported. In this work we present an optimized design of a flow-through ATR cell for transient experiments in the solid–liquid interface and an analysis of the operative limits to obtain intrinsic kinetic information under chemical control.

2. Experimental

2.1. Spectroscopic setup

A stainless steel flow-through ATR cell with small volume and minimized dead volumes was design and constructed. The cell was mounted onto an ATR attachment (Pike Technologies) inside the sample compartment of the FTIR spectrometer (Thermo-Electron, Nicolet 8700 with a cryogenic MCT detector). The bench of the spectrometer was continuously purged with dried air (Parker Balston FTIR purge gas generator) to eliminate CO_2 and water vapor contributions to the spectra. Time-resolved ATR-FTIR spectra were recorded in kinetic and rapid-scan mode at a resolution of 4 cm^{-1} (up to 1 spectrum/0.39 s). The IRE used was a 45° trapezoidal ZnSe crystal, whose dimensions are $80 \times 10 \times 4$ mm, providing 10 internal reflections at the liquid/crystal interface.

Liquids, provided from two separate bottles, were flowed through the cell using a pulse-free peristaltic pump (Ismatec ICP4) located at the end of the cell. A pneumatically actuated three-way valve controlled by a computer software allows to switch the stream of solutions. More details of the experimental setup can be found elsewhere [10]. Carbon tetrachloride (CarboErba HPLC grade, 99%), isopropyl alcohol (Cicarelli, 99.8%), Triton X-100 (Sigma–Aldrich), and deionized water (18 MΩ) were used.

For the CO adsorption experiments, a platinum layer with a thickness of about 20 nm was prepared by vapor deposition. In order to clear the platinum layer, the coated IRE was pretreated ex situ under pure H_2 (50 cm^3/min) at 473 K for 2 h, and purged with He at the same temperature (30 min). Next the Pt/ZnSe was fitted on the ATR cell, and after purging with He, was exposed again to H_2 (5%)/He at 293 K.

Dissolved CO in water was provided from a glass saturator, at controlled temperature, where water could be saturated by bubbling CO, and flowed through the cell using a peristaltic pump located downstream.

2.2. Computational simulation

2.2.1. Modeling and simulation of the cell fluid dynamics

Designing an efficient microfluidic device firstly demands a careful knowledge of the fluid velocity filed in the transport and reaction regions. Therefore we carried out numerical simulations to study the 3D fluid streamlines in the ATR cell, mainly in the entrance/exit regions. In the framework of continuum fluid mechanics, fluid velocity $\boldsymbol{v}$ and pressure p are governed by Navier–Stokes equations [14],

$$-\nabla \cdot \boldsymbol{v} = 0 \tag{1}$$

$$\rho\left(\frac{dv}{dt} + \boldsymbol{v} \cdot \nabla \boldsymbol{v}\right) = \nabla \cdot \left[-p\boldsymbol{I} + \mu(\nabla \boldsymbol{v} + \nabla \boldsymbol{v}^T)\right] \tag{2}$$

Eq. (1) expresses the conservation of mass for incompressible fluids. Eq. (2) expresses the conservation of momentum for Newtonian fluids of density ρ and viscosity μ. Two computational domains containing the fluid were considered and are shown schematically in Fig. 1. The no-slip condition is imposed at the walls, and isothermal conditions are assumed. The flow rate through the cell was imposed by setting the appropriate velocity at the inlet. Flow profile at the inlet was chosen as uniform and relative pressure was set to zero at the outlet.

The numerical simulations presented were performed in PETSc (Portable Extensible Toolkit for Scientific Computation)-FEM (Finite Element Method), which is a parallel code primarily targeted to 2D and 3D finite elements computations, on general unstructured grids [15]. PETSc-FEM provides a set of specialized application programs addressed to a variety of multiphysics problems. In particular, fluid flow computations presented in this article were carried out within the Navier–Stokes module. Further details can be found in [16]. Visualization and post-processing were carried out in Paraview 3.6 [17].

2.2.2. Modeling and simulation of mass transfer in the cell

The 3D calculations described above demand an excessive computational time if one aims to solve the convection–diffusion transport problem of a given species in the full geometry of the cell. Instead, one may take advantage of both the large width/height aspect ratio of cell (∼14), and the fact that the flow is fully developed (see below Section 3.1), which yield a practically unidirectional flow profile throughout the cell. This suitable simplification allows one to perform accurate numerical calculations of transport phenomena in practical times.

Therefore, the following considerations are made to model the convection–diffusion problem in the computational domain shown in Fig. 2: (1) The cell operates at low Reynolds numbers (Re < 5), hence the assumption of laminar flow is appropriate; (2) the fluid velocity profile is uniform in the y-direction, and fully developed in the x-direction (except by the relatively small entry/exit zones), hence the velocity varies in z-direction only; (3) concentration variations in the y-direction are negligible small; (4) no adsorption of species on the IRE is assumed; and (5) dilute solutions are considered.

In this context, the conservation equation for the i species without chemical reaction is given by [14,18]:

$$\frac{\partial C_i}{\partial t} + \frac{\partial C_i}{\partial x} v_x(z) = D_i\left(\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial z^2}\right) \tag{3}$$