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Modelling and optimization of IR cell devoted to *in situ* and *operando* characterization of catalysts

Armando Carías-Henriquez, Stan Pietrzyk, Christophe Dujardin*

Université Lille 1, Sciences et Technologies, Unité de Catalyse et de Chimie du Solide (UCCS), UMR CNRS 8181, Cité Scientifique, Bâtiment C3, 59655 Villeneuve d'Ascq, France

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ABSTRACT

CFD modelling and tracer experiments were performed in order to improve the design of sample holder used for transmission IR experiments in flow conditions.

The complexity of gas velocity field evidenced for the usual circular geometry is avoided with an alternative geometry. A new geometry involving a square pellet, multiple inlets and outlets and specific sample holder proposed in the present study leads to a more homogeneous gas velocity in the vicinity of the catalyst surface as shown by modelling with COMSOL. Experimental measurements of local tracer concentrations in different places of the reactor during transient experiments confirmed more homogeneous tracer distribution in the reactor mainly due to multiple inlets and outlets. Consequences of the presence of dead volumes identified by modelling were also examined and discussed.

1. Introduction

The characterization of catalyst in reaction conditions is widely used at laboratory scale and provides useful information that generally leads to the proposition of reaction mechanism. Infrared spectroscopy is very powerful due to its high sensibility to adsorbed species detection and is applied to investigate reaction mechanism for various applications [1]. Operando conditions are generally required to combine catalytic measurements and simultaneous spectroscopic measurements as suggested by Bañares [2].

Both transmission and DRIFT modes can be applied for IR measurements in heterogeneous catalysis [3–5]. A variety of cells are used for IR studies in the literature and has been reviewed by Peri [6] and Ryczkowski [7]. Generally the specific geometry of the sample required in transmission mode (wafer of catalyst) makes it difficult to obtain ideal plug flow reactor conditions. However few studies deal with the optimization of this category of reactors [8,9].

Recently, Meunier described a possibility to optimize DRIFTS reactors [10]. Their observations demonstrate how an appropriately modified commercial DRIFTS cell can provide pertinent kinetic information based on analyses of gaseous reactants and related surface intermediates [11]. In their reactor a continuous flow of reactants passes through a fixed bed of catalyst. The modifications proposed concern avoidance of the reaction mixture bypassing of the catalysts bed, existing in the original reactor. Thus reaction rates as well as apparent activation energies similar to those previously measured on a tubular reactor could be obtained on a DRIFTS cell [12].

The reactors, original and modified ones, described in paper by Meunier et al. may be considered as plug flow ones, and modelled as such. In the case of transmission IR spectroscopy, several improvements have been recently proposed. Wang et al. developed an inexpensive and simple operando transmission IR cell using a circular self-supported wafer [13]. In the previous version developed by Bell et al. [14], grooves cut on the inside surfaces of the sample holder assured a distribution of the gas flow around the disk. However the geometry of these grooves cut could influence the gas flow distribution.

Tan et al. reported the influence of retention posts in a silicon microreactor [15]. They underlined that the precise flow distribution depends on the exact distribution of the gas. Clear channelling of the inlet gases was evidenced directly to the outlet port in the absence of retention posts. Non-ideality trend was also obtained when only some of the retention posts are present.

Alternately, Yang et al. designed a reactor where the catalyst can be directly pressed into an optically thin tungsten grid and placed in the reactor system in order to minimize internal reactor volume [8].

This paper presents the optimization of similar type of operando reactor, with a thin wafer of catalyst exposed to laminar gas flow parallel to its surface that can mimic reaction on a monolith. The species in the gas phase of the reactor cell and adsorbed at the catalysts surface are typically monitored by means of an Infrared (IR) beam perpendicular to the wafer, while the entrance and exit gas

* Corresponding author. Tel.: +33 328 778 529; fax: +33 320 436 561.
E-mail address: christophe.dujardin@univ-lille1.fr (C. Dujardin).

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phase concentrations are measured by means of quadrupole mass spectrometer (QMS). Such reactor could be used as a transient-operated one-pass reactor, or as a steady-state reactor with gas recirculation.

In our previous works [8,16] we proposed a model of a cylindrical sample support, in which the wafer was considered as a catalytic wall and the gas phase was treated using Navier–Stokes equations (transient convection-diffusion mass transport and steady-state momentum transport, respectively).

Although the modelling of this cylindrical cell performed with COMSOL 3.5a software was found possible and qualitatively correct, it was also shown that the cylindrical geometry of the cell was not optimal. In order to check the accordance between the modelling of the gas flow and mass transport modelling against experimental data which is required before any kinetic measurements, two types of sample holder were compared with two alternative geometries: a circular pellet in a cylindrical holder and a square pellet with a rectangular holder. Pulses of N_2O were injected in a continuous flow of He and its concentration was measured by IR and MS techniques with an inert wafer. The results have been compared with COMSOL modelling results. Furthermore, the tracer's concentration *vs.* time was measured in the reactor in selected areas in order to compare local concentrations during pulsing of N_2O.

2. Experimental

2.1. Materials

A γ-alumina obtained by sol–gel method using alkoxide precursors was used as reference material [17]. 7 mg of alumina was finely crushed and then pressed into pellet of 2 cm^2 (diameter 16 mm) under a pressure of 100 MPa/cm^2. Alternately, the square pellet (5.2 mg) was obtained from circular one by cut in order to obtain a square of 11 mm × 11 mm. Pellets were placed in the corresponding sample holders (circular or square) and then loaded in the IR cell and connected to an automatic setup for gas flow and valve control.

2.2. Reactors

Two different reactors (sample holders) were used. The first one made of stainless steel (Fig. 1A) is identical to that used previously [8,9]. The cell space containing the round pellet is cylindrical, the coaxial single gas inlet and outlet are situated on the opposite sides of the cell, and made of 1/8″ stainless steel tubes (external diameter).

The second reactor is made of boron nitride because of high thermal conductivity and the fact that boron nitride is more tender than stainless steel and thus allows the manufacture of complex design. In the second reactor presented in Fig. 1B, the internal cavity

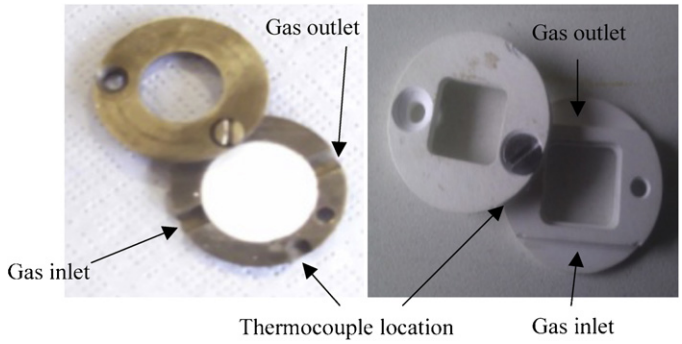

Fig. 1. Geometry of sample holders using circular pellet (A) and square pellet (B).

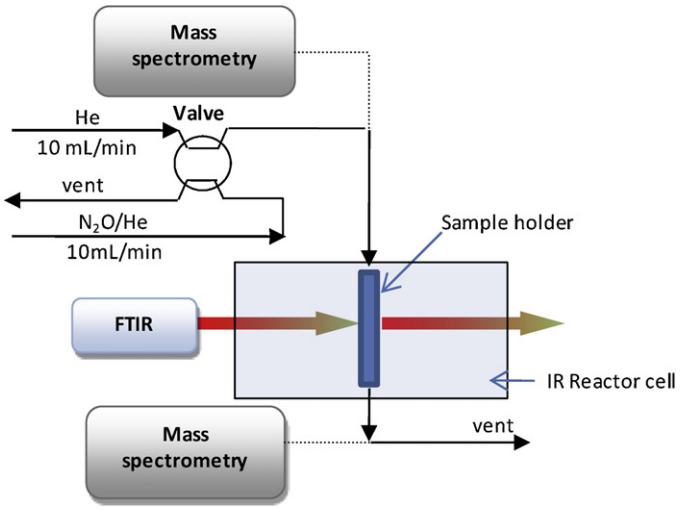

Fig. 2. View of the experimental setup.

of the cell and the pellet are square, and the inlet and outlet are constituted each of 2 × 6 holes of 0.6 mm diameter arranged in two parallel ranges. This geometry was chosen as a result of previous experimental and modelling work with the first reactor. It was expected to assure better homogeneity of gas phase concentrations in the vicinity of the pellet surface and furthermore allow a future modelling in 2D approximation instead of actual 3D necessary with the first reactor, with an obvious reduction of computing time.

2.3. Instrumentation

A scheme of the setup is shown in Fig. 2. A series of rectangular pulses of N_2O in He (2815 ppm), width 2 s, was introduced to the carrier He flow of 10 mL/min, at 25 °C and atmospheric pressure by means of a 4-way valve. The delay between two pulses was 5 min. The gas flows were controlled by means of mass flow regulators Brooks Series S.

N_2O concentration at the entrance and exit of the reactor were measured by means of a quadrupole mass spectrometer Omnistar from Pfeiffer. Signals at $m/z = 4$ and 44 were recorded for respectively He^+ and N_2O^+. After each sequence, a calibration of mass spectrometer response towards N_2O was performed.

The IR absorption of sample was measured by means of a Thermo 6700 FTIR spectrometer in the axis perpendicular to the wafer as described by Lesage et al. [18]. In some experiments, the alumina wafer was replaced by opaque plates with variously situated holes of 1.8 mm diameter in order to determine the tracer gas concentrations at different places in the cell. The locations of holes corresponding to each local concentration measurement are presented in Fig. 3.

2.4. Modelling of the gas flow and transient mass transfer in the reactors

2.4.1. COMSOL modelling

Modelling of the cell was performed by means of COMSOL Mutiphysics software, versions 3.5a and 4.0, with chemical engineering module (3.5a), using 3D geometry. Since Reynolds number estimated in different points of the apparatus were low, of the order of 1 or less, gas flow was treated as laminar. The gas flow was modelled first using steady-state incompressible Navier–Stokes equations in order to reduce the computation time. After that, transient analysis of convection and diffusion was performed for the gas velocity field determined in the first step.