



A versatile Carberry-type microcatalytic reactor for transient and/or continuous flow operation at atmospheric or medium pressure



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HIGHLIGHTS

- A novel Carberry-type well-mixed catalytic microreactor is presented.
- Both batch (transient) or continuous operation is feasible.
- Carefully controlled temperature and pressure (up to 3 MPa) conditions achievable.
- Continuous measurement of gas phase composition by mass spectrometry is provided.
- The device performance was validated by comparing measured reaction rates with literature data.

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ABSTRACT

A novel catalytic reaction device featuring a Carberry-type well-mixed microreactor built inside a medium pressure leak valve is presented. The complete reaction system allows a broad range of kinetic reaction engineering and heterogeneous catalysis studies for both batch (transient) and continuous operation. Carefully controlled temperature (± 0.2 K) and pressure (up to 3 MPa) conditions can be achieved. The continuous sampling of the reacting mixture permits instantaneous evaluation of the gas phase composition.

The device performance was validated by comparing methanol synthesis reaction rates for H_2/CO_2 mixtures obtained under transient conditions using this catalytic microreactor with steady-state kinetic rate expressions obtained using a conventional plug-flow microreactor employing the same Pd–GaOx/SiO₂ catalyst. Excellent agreement was found.

The reaction was also studied using a more active commercial methanol synthesis catalyst to assess the impact of heat and mass transfer resistances. For the full range of process conditions that was tested, the microreactor operated well under the kinetic regime.

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1. Introduction

The use of heterogeneous catalytic reactors for reaction engineering studies and catalyst screening at the laboratory scale is essential. In both cases, kinetic and mechanistic information must be extracted from experiments in which the desired catalytic reaction proceeds together with secondary reactions, physicochemical equilibria, and/or transport processes [1]. A careful choice of operating conditions and complementary studies can eliminate many of these confounding variables, but the type of reactor used and its size and geometry are key factors in minimizing the mass and energy transfer resistance to obtain *intrinsic* chemical kinetic data. In this regard, novel and continued efforts appear, using either particular techniques (e.g., SSITKA [2]) or special designs [3,4] for transient experiments.

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Plug-flow (PFR) and continuous flow stirred tank reactors (CSTR) are the traditional tools for kinetic studies under steady-state conditions. Neglecting economic issues (such as those related to isotopic studies), these devices must be operated at low conversion to avoid concentration or temperature gradients at the expense of higher experimental error in the analytical measurements [5]. Discontinuous (batch) reactors, however, are not widely used in heterogeneous catalysis studies due to several drawbacks, although each can be resolved:

- Catalyst deactivation may complicate the analysis. Stabilization of the catalyst prior to the batch experiment and between runs can resolve this issue.
- Batch reactors intrinsically operate in a transient regime, which means that a steady-state composition of chemisorbed reactants and intermediates on the catalyst surface may not be reached. The previous strategy can be employed here, also.

- If only the final composition is measured, only average molar fractions are available for calculations. Periodic extraction or continuous sampling of minute gas amounts can minimize this issue.
- In reactions in which there is a stoichiometric change in the number of moles ($\Delta v \neq 0$), such as in the Fischer–Tropsch process, methanol or higher alcohol syntheses, or methanation, there is an intrinsic continuous pressure change. This can be accounted for by using differential conversion data and/or employing internal standards.

Despite these disadvantages, batch reactors allow performing chemical reaction engineering experiments with very low reactant consumption and can additionally be used to extract unique information related to the catalyst response under non steady-state, transient conditions [6–8].

Under these premises, a versatile batch/flow reaction device was built. The core of the unit is a well-mixed ('gradientless') Carberry-type microreactor that suppresses all gradients in the gas phase, thereby maximizing heat and mass transfer between phases [9]. The device is similar to others previously reported in the literature [10,11] but offers some advances in versatility (it can be operated as either a CSTR or a batch reactor) and operating pressure range (it can be evacuated/flushed under moderate vacuum and operated at up to 3 MPa). The reaction device was tested and validated using a demanding reaction system, the selective synthesis of methanol via the hydrogenation of carbon oxide(s), as a model reaction. Many of these reactions must be conducted at moderate to high pressure to overcome thermodynamic constraints and yield a significant conversion.

In the following sections, design details and operating protocols of the microreactor are presented together with data validation employing two different methanol synthesis catalysts, $\text{Ga}_2\text{O}_3\text{-Pd/SiO}_2$ and $\text{CuO/ZnO/Al}_2\text{O}_3$.

2. Experimental

2.1. Microreactor design and features

Two identical small volume cylindrical compartments ($\sim 37 \text{ cm}^3$ ea.) made of 316 stainless steel enclosed in a thermostated oven and interconnected by a high rating (high purity, high pressure-high vacuum, high temperature) bellows valve,

constitute the core of the reaction device (Fig. 1). For the batch operating mode, the first compartment acts as a premixer/homogenizer of the reaction mixture. The composition of this mixture can be adjusted at will using a dosing manifold, as detailed below.

Each compartment accommodates a small, removable, magnetically stirred Carberry-type spinning basket [12,13] that can be filled with crushed and sieved particles of the catalyst to be studied and (optionally) with a particulate, inert solid in the premixer. The structure of the spinning device comprises a 316 SS central axle, four baskets made of 250 mesh stainless steel cloth, a horizontal gold-plated mild steel bar on the bottom and a removable cross of top-bladed basket lids. The blades are flat and welded at 45° to ensure good mixing and gas recirculation. The central axle rotates freely by means of two ball bearings. A flexible metal 'spider' made of pure silver gently presses the upper ball bearing against the axle, thus allowing smooth, effortless rotation. All of the removable components, as well as the internal parts of the premixer and the reactor, are gold plated. Magnetic stirring is achieved by means of high temperature $\text{Sm}_2\text{Co}_{17}$ permanent rotating magnets ($T_{\text{max}} = 723 \text{ K}$, Electron Energy Corporation, Landisville, PA, USA) driven by variable speed motors.

The premixer and the reactor are constituted by two cylindrical pieces. Both bases are mechanized from stainless steel Conflat type flanges (CF 275). The upper portion of the premixer is an inverted cup, whereas the upper part of the reactor is a bakeable (up to 723 K), high-pressure variable leak valve (AVAC, Redwood City, CA, U.S.A.) that can sustain up to 34 bar with ultra-small gas leaks ($1 \times 10^{-8} \text{ Torr}^{-1} \text{ s}^{-1}$; $3 \times 10^{-13} \text{ mol s}^{-1}$ at 523 K). Sealing is achieved by electrolytic copper washers. The bases of both compartments are bolted to aluminum heating blocks inside which heating cartridges are placed. Thermostatic conditions can be precisely set by means of Pt100 thermo-resistances and independent PID temperature controllers. Unless otherwise noted, inlets and outlets are standard welded VCR fittings with metal seals to grant maximum flexibility with regard to pressure or vacuum operation of the units.

As indicated in the Introduction section, the microreactor can operate either in batch or continuous flow modes. The latter is indispensable for catalyst pretreatment, preconditioning or stabilizing/aging procedures. To this end, a soft contact, gold-plated (T-type) piston valve with Kalrez seals, integrated to the reactor compartment base, was designed (Fig. 1).

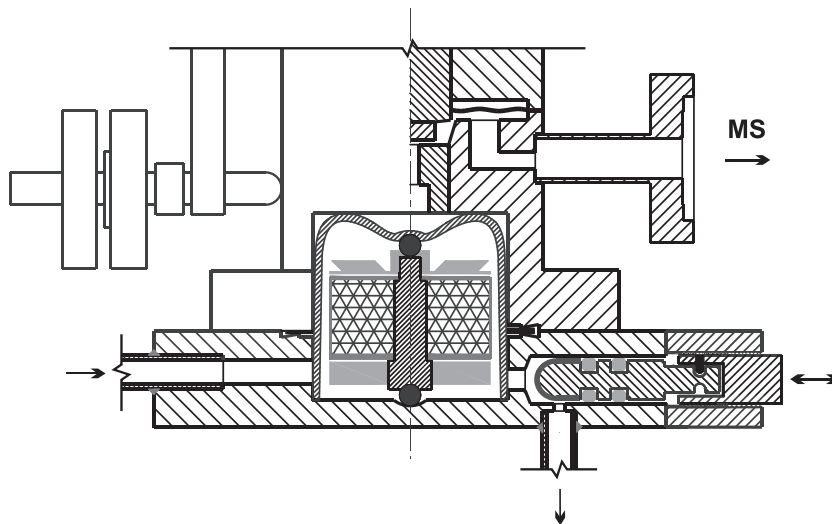


Fig. 1. Scheme of the microreactor and internals (For details, see [Supplementary Information](#)).

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