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# Design and characterization of a stagnation flow reactor for heterogeneous microkinetic studies

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## HIGHLIGHTS

- Alternative reactor to integrate Surface Science and Industrial catalysis.
- Development of a flexible, yet simple reactor for catalytic film testing.
- Detailed simulation reveals conditions for transport limitation interferences.
- Heat transport in the gas phase is more critical than diffusion limitations.
- Unexpected predictions on dominant role of heat transfer confirmed by experiments.

## ARTICLE INFO

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## ABSTRACT

By modelling of mass, momentum and thermal energy transport we critically investigated the design of a flexible testing cell. Its purpose is carrying out reactivity tests at high pressure ($\geqslant$1 bar) on flat, disk-shaped active surfaces, under continuous gas flow. We revisited the stagnation-point flow arrangement to quantitatively evaluate the potential and the critical factors affecting the experimental information achievable. We investigated the constructive and the operating parameters. Specifically, geometry, contact time, temperature, rate of surface reaction, reactant diffusivity, carrier thermal conductivity, and heat of reaction were parametrically varied. Simulations confirm that reactions can become limited by reactant diffusion at high temperature (i.e. fast reactions), in a perfectly isothermal cell. However, the heat of reactions can easily distort the surface temperature distribution, as evidenced by 2D simulations; thus, the flow structure in the testing cell and the carrier heat conduction become the controlling factors, determining the reaction extent. Finally, a prototype was built and operated using $H_2$ oxidation on a polycrystalline Pt disk, as probe catalyst and reaction. Measurements confirm the consistency of the simulation study, revealing the critical role played by the unexpected local temperature distribution on the active surface, largely prevailing on any mass diffusion limitation in determining the apparent activity of the surface.

## 1. Introduction

Progress in the understanding of catalytic mechanisms takes place through measurements on either well defined and ordered surfaces, or on powders. In the first case, surfaces are single crystals cut along low Miller index planes or more complex structures build upon them [1]. Model surfaces are expected to provide fundamental understanding on the surface chemistry, supporting the design of actual catalysts for industrial applications. Powders in contrast are characterized by low coordinated sites (steps, kinks, vacancies and other defects), that can dramatically change the surface mechanism, as suggested by several structure-reactivity studies [2]. The different activity of ideal surfaces vs. powders is sometimes referred as the structure gap [3]. It justifies some divergence of methods and practical conclusions that do not support an effective transfer of knowledge from the scientific to the industrial communities.

Structure gap can be partially overcome using single crystal surfaces cut along high Miller index planes [3,4]; having steps and kinks, they approximate the defective industrial catalyst surfaces. Unfortunately, only one type of defect at a time can be studied by this technique. Other Surface Science techniques allow the growth and self-assembling of thin films on nanostructured templating surfaces [5,6], aimed at controlling the active sites atomic structure, approaching the complexity of industrial catalysts.

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In addition, the investigation on model surfaces is carried out in ultra-high vacuum (UHV) [5,7,8], determining a pressure gas. Attempts to overcome it are limited by the pressure allowed by the measurement instruments, so that 'near ambient' versions were developed. Still, the high pressure claimed is just relatively high, with respect to UHV, but in practice well below 1 bar, in the tenths of mbar range [10], as required to use low energy electron and ion-based experimental techniques without undue interference from gas phase scattering.

The model surfaces are almost exclusively prepared as samples that are macroscopically flat, not powders [11]. The samples can be from mm to cm in size; often it is a surface film that brings the chemically specific activity. The reactivity of model surfaces is determined with appropriate testing devices, typically UHV chambers, possibly with static atmosphere, by carrying out local measurements of surface events [1,12]. We may call the limitation in the testing devices the reactor gap. To further support the indication of Surface Science techniques and link them to actual, macroscopic activity, a significant step would be the possibility of testing the global reactivity of such model surface samples. Global, or integral reactivity of an active surface is meant to be the result of the catalytic function over the whole surface, as opposed to local measurements. Global reactivity measurement requires appropriate testing devices (i.e. reactors) operating on model surfaces at higher pressure ($\geqslant 1$ bar), higher concentration of reactants and possibly under flow conditions. We believe that the overall reactants conversion and selectivity given by a model surfaces, at industrially relevant conditions, is a macroscale confirmation of the microkinetic models. Macroscale behavior of model surfaces must prove whether the surface mechanisms actually determine a meaningful, complete catalytic path for the reaction under study, rather than just a few, local steps in the mechanism, possibly changing within a complete reaction mechanism. In addition, a consolidated concept of catalyst as a species with invariant properties that can facilitate reactions, but it is not affected by the environment is being questioned by modern approaches and evidences [9,13]. That urges the investigation of the surface reactivity in a representative, not idealized, environment. Measuring the global reactivity of model surfaces is also expected to contribute to the development and validation of microkinetic models of surface reactions, profitably complementing the detailed information of DFT calculations [13–16]. Macroscopic testing of pure metal surfaces in flow reactors has been done in the past, mostly confined to noble metals foils [17–19] or wires [20,21], typically without a precise control of the surface crystal structure. While simple in principle, the quantitative analysis of such experiments may yield unexpected results [22]. We believe that the detailed characterization of the testing device is a perquisite to extract meaningful information from model surfaces.

Here we present a systematic numerical analysis of the stagnation flow configuration, which is a general flow arrangement that nicely fits the testing of disk-shaped, flat model surfaces for global activity. Its modelling [23,24] has been developed into standard applications [25,26] under some simplifying assumptions discussed below, aimed at developing and validating microkinetic models. Still, contradictory experimental results that we obtained suggest that a thorough understanding of its operation and critical features requires additional investigation. We used a model reaction to numerically assess the possible role of heat and mass transfer limitations at isothermal or adiabatic operation, as discussed also by Others [27]. Through parametric studies, we designed a versatile testing cell, for any disk-shaped reacting surface.

The experimental validation on $H_2$ oxidation on Pt as model reaction proves that mass diffusion is not the controlling process. The temperature spatial distribution turned out to be the key determining factor, severely distorting the apparent activity measurements. We believe that these results can explain previous discrepancies in the Literature, where the light-off temperature of $H_2$-air mixtures differ by more than 50 K.

## 2. The stagnation point flow (SPF)

A heterogeneous fluid-solid reaction based on a disk-shaped, planar surface can be effectively carried out under stagnation flow, as shown in Fig. 1. The arrangement has been used since a long time for thin, epitaxial film growth, to be used in electronic and optoelectronic applications [28]. It has been also suggested and widely used for catalytic studies [17,24,31]. In its original design, the disk is often rotating, and the gas is fed in the chamber well above the surface, at a distance that can be several disk diameters [28]. The deposition of epilayers was found to be affected by the gas dynamics on front of the surface, because of mass transfer limitations. Experimental [28,29] and computational studies [29,30] have been carried out to visualize, identify and predict the regimes that develops in front of the solid surface. Gas has been fed by a centered jet (a very common industrial configuration), swirling jets, and porous layers. Stable and unstable regimes have been observed, and three reference flow arrangements (rotational, buoyant, and plug) identified. Flow maps have been developed to predict the prevailing regime, based on Grashof and Reynolds numbers [29]. The optimal configuration aims at developing a plug flow over the surface, with the minimum boundary layer thickness, to improve mass transfer rates to the surface. It can be obtained by feeding the gas through a porous diffuser, possibly larger that the disk, at fairly short distance for the surface (fractions of disk diameters), at a flow rate large enough to contrast buoyancy-driven recirculations [30]. Such a design aims at an effective and uniform transport of gas reactants to the surface, for its regular growth.

Here we suggest a variation of this arrangement, allowing to measure the activity of a catalytic surface by changes in the gas composition. In addition to an effective, stable and reproducible contact with the surface, most of the gas must reach the surface, to measure appreciable variations in its outlet composition. Accordingly, we focused on the centered arrangement shown in Fig. 1, right, where the inlet mixture is focused at the center of the surface and spreads radially towards the surface periphery. We call such a flow configuration towards a reactive surface a *Stagnation Point Flow Reactor* (SPFR). Guiding the divergence of the flow (see Fig. 2) further allows to keep it parallel to the surface, at sufficiently high velocities to dominate any buoyancy effect and achieving short catalyst contact times. The momentum-dominated, parallel, diverging flow is also expected to be better described by simpler reactive flow models, directly involving surface chemistry, of any complexity.

The stagnation flow configuration using a distributed inlet can be simulated with restrictive assumptions, by a 1D model, using a suitable change of variables [24], [32]. The 1D domain can be extended to include a porous catalytic layer [33]. In this study we focus on model catalyst that are non-porous; only external mass transfer is meaningful. Implementations of the 1D model that allow for detailed surface chemistry are available both in the CHEMKIN [25] and Cantera [26] simulation environments. To account for the actual arrangement of the inflowing stream, without any restrictive assumption, we simulated the SPF with a flexible and widely validated computational fluid dynamics (CFD) codes. We used one *COMSOL Multiphysics*, [34] to investigate the effective role of the inlet size, as well as other design parameters, preliminary to the construction of a test cell. The Comsol simulation code can also be interfaced with Cantera [35], for kinetic studies using detailed surface chemistry. Thus, it becomes a useful tool for activity measurements analysis and interpretation, in addition