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What happens in a catalytic fixed-bed reactor for *n*-butane oxidation to maleic anhydride? Insights from spatial profile measurements and particle resolved CFD simulations

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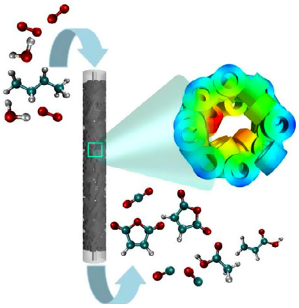
HIGHLIGHTS

- *n*-Butane oxidation under industrially-relevant conditions was investigated.
- CFD models were validated and applied for knowledge-based reactor optimization.
- High resolution species and temperature profiles were measured.
- Structuring reactor wall profile can eliminate hot-spot and increase selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

Industrial catalytic reactors are made of steel, operate at high temperatures and pressures and contain hazardous chemicals. What happens inside remains hidden. Reactor optimization requires costly trial and error or is based on simplified mathematical models employing more or less accurate transport correlations and reaction kinetics. In the present work a pilot-scale fixed-bed reactor was developed for measuring concentration and temperature profiles for *n*-butane oxidation to maleic anhydride on vanadyl pyrophosphate catalyst pellets under industrially-relevant conditions. The reactor was equipped with five heating zones. The reactor was modeled by particle-resolved computational fluid dynamics. The catalyst bed was created by discrete element simulation and the result was validated by comparison with experimental radial porosity profiles. Catalytic chemistry was included by a kinetic model of intrinsic reaction rates. Transport resistances and packing deviations were lumped in reaction rate multipliers determined by fitting the model to profiles measured at a uniform reactor wall temperature. Simulation results reveal strong inhomogeneities inside the bed. A hot-spot develops at uniform wall temperature. At this hot-spot temperature differences of 40 K exist on one and the same pellet with negative impact on maleic anhydride selectivity and catalyst lifetime. An optimized wall temperature profile was derived by combining knowledge from the experimental profiles at uniform wall temperature and the CFD results. A gradual increasing temperature was predicted by the model to eliminate the hot-spot and increase integral maleic anhydride selectivity at constant *n*-butane conversion. This prediction was confirmed by experiment. At 80% *n*-butane conversion the maleic anhydride selectivity could be improved by 2%. Facing the scale of the

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process, this improvement translates into significant *n*-butane savings, reduced CO_x emissions and increased revenue.

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1. Introduction

n-Butane oxidation to maleic anhydride (MA, Eq. (1)) is an important catalytic oxidation process. In 2015 the annual worldwide MA consumption amounted to 2.8 Mio metric tons [1]. One popular process variant employs multi-tubular fixed-bed reactors filled with catalyst pellets of vanadyl pyrophosphate (VPP) cooled by circulating molten salt [2,3]. The fixed-bed process runs typically at 80–85% *n*-butane conversion achieving an overall MA yield of about 57–65% [4]. This unsatisfactory MA yield motivates chemists and chemical engineers to improve reactor and catalyst performance. In view of the large scale of the process even small improvements translate into significant revenue [4].

$$C_4H_{10} + 3.5O_2 \rightarrow C_4H_2O_3 + 4H_2O \quad \Delta H^{\circ}_{R,298K} = -1240\ \frac{\text{kJ}}{\text{mol}} \qquad (1)$$

Radial heat transfer limitations require rather small reactor tubes for this exothermic reaction (Eq. (1)). Typical inner diameters are on the order of a few centimeters. Pressure drop determines size and shape of the catalyst pellets. Hollow cylinders of bulk VPP with an outer diameter of 5–6 mm are often used. Therefore, industrial catalytic fixed-bed reactors for *n*-butane oxidation are characterized by small D/d ratios (ratio of reactor diameter D to pellet diameter d). The random packing of catalyst pellets in reactor tubes fitting only a few particles across the tube diameter leads inevitably to pronounced local inhomogeneities. The interactions between flow, heat and mass transfer and catalytic reactions in such highly inhomogeneous packings are of particular interest and subject of this work. High resolution spatial measurements of species and temperature inside the reactor combined with particle resolved CFD modeling of chemistry and flow is a promising approach to understand the physical and chemical processes inside a catalytic *n*-butane oxidation reactor and provide a methodology for knowledge based optimization of this important industrial process.

The conventional way to study catalytic reactions and to test new catalysts in the laboratory is the ‘in-out’ approach. If concentration and temperature gradients over the catalyst bed are kept small, it is sufficient to analyze what is flowing in the reactor and what comes out of the reactor. A thermocouple inside the catalyst bed delivers a representative temperature value. In pilot scale reactors operating at industrial conversion levels concentration and temperature gradients are naturally pronounced. ‘In-out’ species analysis and a single temperature reading from the center of the fixed-bed are not sufficient to resolve the gradients occurring inside the reactor. Side sampling ports equipped with thermocouples provide some spatial resolution but the point density in regions of steep gradients is often insufficient and wall effects compromise the representativeness of the measured concentration and temperature values.

In recent years movable capillaries with side sampling orifices have been used to measure species profiles through laboratory fixed-bed reactors with submillimeter resolution [5,6]. Temperature sensors or spectroscopic fibers placed inside the capillary provide temperature profiles and spectroscopic information about the catalyst. In the present work this methodology has been taken to pilot-scale for the first time. A pilot-scale profile reactor was designed and built for studying *n*-butane oxidation on vanadyl pyrophosphate (VPP) pellets under industrially relevant conditions. The fixed-bed reactor has the same diameter ($D = 2.1$ cm) as a single tube in an industrial multi-tubular reactor. VPP pellets of industrial dimensions were used as catalyst packing. The catalyst bed was 50 cm in height to keep gas flow rates within bounds.

To interpret the measured species and temperature profiles and to allow for model-based optimization the reactor was modeled by means of particle-resolved three-dimensional computational fluid dynamics (CFD) [7]. A particle-resolved CFD model was chosen over the more common pseudo-homogeneous models because transport correlations in the ‘pseudo-’ model family become inaccurate in fixed-beds at small D/d ratio (below 10), especially for heat transfer and highly exothermic reactions [8,9]. Furthermore, pseudo-homogeneous or heterogeneous models are unable to reproduce spikes and dips observed in the experimental profiles due to the very inhomogeneous packing [10] and to separate reaction effects from dead zones or bypass flow.

After the pioneering work of Dixon et al. [7,11,12] strong efforts have been made to develop CFD modeling of fixed-bed reactors further. Active fields of research include computer-generated packings [13–15], meshing strategies [16–18], flow and pressure drop [13,19], heat transfer [11,20–22], surface reactions described by microkinetics [23–25], methods of incorporating pore diffusion and reaction in pores [26–29] as well as computational algorithms [30].

Several factors affect the prediction performance of CFD simulations of fixed-bed reactors [31]. One is the computer generated random packing which has to match the experimental packing in terms of bed density and porosity within statistical bounds. The Discrete Element Method (DEM) is one widely applied method for particle simulations and has been validated to predict the radial porosity profiles of spherical [13] and non-spherical packings [22] at various D/d ratios [32]. Even if physical properties required as input for DEM simulations are unknown or uncertain, e.g. friction coefficients of the catalyst pellets [32,33], their influence on the final packing is not too pronounced unless particle-fluid interactions or particle breakage are goal of the simulation. In fact it becomes common practice to take these parameters as calibration factors to reproduce the experimental porosity profiles [15,32,34]. The second factor is meshing which influences void fraction, pressure drop and heat transfer [16,19]. The third and usually most important factor is the kinetic model [35]. Most published CFD simulations of fixed-bed reactors use microkinetics for surface reactions [23,29,36]. The model prediction is sensitive to the value of the active site density and discrepancies between experiment and simulation often result because the active site density of the used catalyst is different from the value in the microkinetic model. Also this parameter is often tuned for the simulations to match the measurements [10].

Microkinetic models consisting of sequences of elementary steps are most reliable for metal catalysts with simple active sites, e.g. single surface atoms or monoatomic steps, and work best at conditions where the mean field hypothesis applies, e.g. at high temperatures. For *n*-butane oxidation on vanadium phosphate catalysts no reliable microkinetic model exists. Kinetic models comprising power rate laws and Langmuir-Hinshelwood-Hougen-Watson type rate expressions do exist [37] and seem more applicable to this rather complex catalytic reaction because catalyst properties are lumped together in model parameters which are obtained from fitting the model to kinetic data. Consequently a kinetic model with experimentally determined parameters was used in the present work. The kinetic model augments the widely applied reaction scheme to incorporate acrylic and acetic acid in the network. The kinetic measurements were done with crashed catalyst in a classic kinetic test reactor and delivered intrinsic reaction rates with negligible impact of mass and heat transfer. Since the profile measurements were conducted with full-size catalyst pellets, effectiveness factors had to be introduced into the CFD model to take pore diffusion into consideration [26]. Due to the unknown pore structure of the industrial catalyst pellet, effectiveness factors were adjusted in the kinetic model such that for one set of operation conditions (training set) the predicted temperature and species profiles match the experimental profiles as closely