Development of a multi-layer microreactor: Application to the selective hydrogenation of 1-butyne

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ABSTRACT

A multi-layer microreactor (MR) was especially developed to assess the effects of the intensification of liquid-phase selective hydrogenation of 1-butyne (BY). The behavior of the system is described and the results of the regression of experimental data are reported. Various MR configurations, differentiated by the number of catalyst layers were constructed. A commercial Pd/Al$_2$O$_3$ catalyst, crushed and sieved to 37–44 μm particle size, has been tested. The reaction was carried out in liquid phase, at three levels of temperature (35, 44 and 60 °C), and covering a range of hydrogen partial pressure of 1.2–5 bar. The kinetic expression used to analyze the experimental data was based on an elementary step mechanism. Fitting of the kinetic parameters allowed to reproduce the experimental results within an average deviation of 3.7%. The results presented in this study are compared to experimental data obtained previously on the same commercial catalyst, but using the original 2.3 mm spherical pellets packed in a conventional fixed bed reactor (FBR). It is concluded from such a comparison that the measurements carried out in the MR are free from diffusion limitations and that the evaluation of such effects in the FBR was satisfactorily performed.

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1. Introduction

The purification of C4-rich cuts, mainly from Fluidized Catalytic Cracking, for the industrial production of high purity 1-butene (1BE) is carried out by selective hydrogenation of 1,3-butadiene (BD) and acetylenic compounds, typically 1-butyne (BY), on Al$_2$O$_3$ supported Pd catalysts [1]. Commercial catalysts are of egg-shell type. High purity 1BE is used in the production of polybutenes and as co-monomer for low-density polyethylene. Current technologies employ catalytic fixed beds with cocurrent flow – either down or upflow – of the liquid hydrocarbon mixture and hydrogen [1]. Operating temperatures are between 20 and 60 °C; total pressure within the range of 8–20 bar to operate with hydrocarbons in liquid-phase.

BD and BY concentrations in the raw stream usually reach around 1 mol%. The target of selective hydrogenation for 1BE purification is to reduce the amount of impurities to about 20 ppm, with minimal loss of 1BE.

We previously verified [2–4] that reactions proceed under strong diffusion limitations inside the active shell of the catalyst particles, causing significant losses of the substance to be purified, 1BE. Although the use of slurry reactors with sufficiently small catalyst pellets can reduce diffusional limitations, the industrial application is inappropriate due to costly filtration steps that would be necessary.

Although many studies on selective hydrogenation on Pd have been reported in the literature, most of them focus on qualitative aspects such as the effect of metallic particle size, presence and type of promoters, identification of product distribution, reaction mechanisms and catalyst deactivation, as caused by oligomer formation on the catalytic surfaces [5,6].

As discussed by Alves et al. [4], the development of kinetic expressions and parameter estimation has been scarcely undertaken, and in most instances the range of experimental conditions has not been wide enough for the purpose of simulating or sizing industrial reactors

We carried out a complete kinetic characterization of the reactions on a commercial egg-shell catalyst [3,4,7,8]. Specifically for the hydrogenation reaction of BY, Alves et al. [8] presented a kinetic model and the estimation of the corresponding parameters, covering a temperature range of 27–62 °C. Experiments performed

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Table 1
Catalyst features [23].

Shape	Sphere	Specific surface area of Pd	$0.55\,m^2/g$
Type	Egg-shell	Metal particle size	3.6 nm
Diameter	2.3 mm	Dispersion	27%
Bulk density	$1150\,kg/m^3$	Tortuosity factor	1.5 ± 0.6
Active shell volumetric fracction	0.49	Mean pore radius	$37 \pm 6\,nm$
Pd load	0.2% w/w	Active shell thickness	0.23 mm
Specific surface area BET	$70 \pm 20\,m^2/g$	Porosity	0.4

until almost 100% BY conversion (i.e., when BY in the mixture reaches around 20 ppm) allowed identifying the (−1) and zeroth-order regimes that arise in the course of BY consumption.

For the analysis of any catalytic reactor it is desirable to have an experimental tool to provide reliable kinetic information in order to determine intrinsic kinetic parameters without the potential masking effect caused by resistance to heat and mass transport. In this sense, the microreactors are an interesting option to study this reactive system in the laboratory. These devices feature fluid channels with lengths in the millimeter-to-centimeter range and cross-sectional dimensions in the sub-micrometer to sub-millimeter range [9–11]. Due to these small dimensions, microreactors have high surface/volume ratios (in the order $10^4\,m^2/m^3$) that result in improved heat and mass transfer characteristics, critical for carrying out chemical reactions efficiently [12–14].

The integration of a solid catalytic phase (heterogeneous catalyst) in microreactors is a challenging task. Conventionally, it is achieved by two methods:

a) By using a micro packed-bed of powdered catalyst [15–17], or
b) By using a thin layer of catalyst coating on the inner walls of microchannels [18–20].

These two alternatives are not exempt from drawbacks, since a powdered catalyst micro packed-bed might result in high pressure drops along the length of the reaction-channel, whereas a thin catalyst coating usually fails to utilize the entire volume of the reactor channel effectively.

In this work, the behavior of an experimental microreactor (MR) developed to study the intensification of selective hydrogenation of BY on milled samples of a commercial Pd/Al₂O₃ catalyst, and regression of experimental data are described. These results are contrasted with those obtained in tests performed in a conventional fixed bed reactor (FBR), in order to verify their consistency and highlight the difference between the two systems regarding the difficulty to obtain the correct experimental data.

2. Experimental

2.1. Materials

The tests were performed on a commercial catalyst Pd loading of 0.2 wt%. The results of the characterization of the catalyst are shown in Table 1.

The commercial catalyst was crushed and sieved to 37–44 μm in the experiments performed with the MR. Previous measurements in the FBR were conducted with the catalyst in its original form, spherical pellets of 2.3 mm diameter with an active shell 0.23 mm thick (egg-shell configuration).

H₂ (99.999%) and N₂ (99.999%) were provided by Linde-AGA. BY (99.999%) and n-Propane (99.999%) were provided by Alphagas. n-hexane (95% HPLC, provided by UVE) served as inert solvent. For assembling the reactor, commercial nylon membranes were used (0.1 mm thick, with a pore diameter of 0.8 μm) (provided by OSMONICS).

Before each run, the compounds fed to the experimental system were purified as described in the next paragraph. The main objective of the purification procedure was to minimize the presence of moisture in the reaction mixture, since it severely impaired catalyst activity [2]. To this purpose, BY, propane and n-hexane were fed after flowing through individual beds of 4A molecular sieve (UOP) and a guard-bed loaded with the same catalyst as used in the experiments. H₂ and N₂ were purified from water and oxygen by passing the streams through a guard-bed followed by a bed of 4A molecular sieve and an oxygen trap (Oxy-Trap, Alltech).

2.2. Experimental set up

Batch experiments regarding the unsaturated hydrocarbons were performed using the experimental setup whose scheme is shown in Fig. 1.

The 100 ml-stirred vessel (Autoclave Engineers EZE-Seal) was used for loading the initial hydrocarbon mixture, feeding H₂ continuously, and maintaining the liquid saturated with H₂ during the runs. The vessel was furnished with an impeller that allows the headspace gas to be dispersed into the stirred liquid. A control tower (Autoclave Engineers CT-100) allowed setting the agitation speed (up to 3000 rpm) and temperature control by means of an electrical heater that encloses the vessel. Gas and liquid samples were taken off by means of two valves connected to the vessel. The agitation speed in the stirred vessel was set at 2000 rpm. It was confirmed that at 2000 rpm the mass transport between the swarm of bubbles and the liquid is efficient enough to saturate the latter with hydrogen at reaction conditions. A magnetically driven gear micropump (Micropump 200) was used to recirculate (700 ml/min) the reaction mixture at high rate from the stirred vessel to the external reactor and back to the vessel.

Apart from the desired unsaturated hydrocarbons, n-hexane was used as an inert solvent to facilitate the manipulation of the samples analyzed chromatographically. Also, a certain amount of propane was used for independent control of hydrogen partial pressure (p_{H2}) and total pressure. The reactor, sketched in Fig. 1, represents the MR used in this study or the FBR previously used.
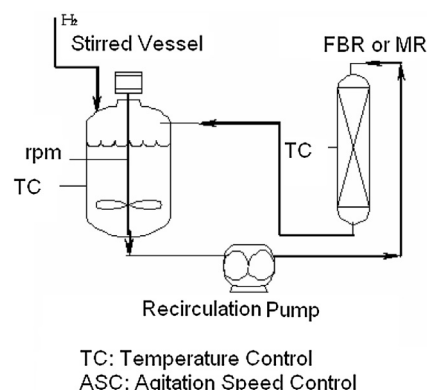

Fig. 1. Scheme of experimental setup.