Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Continuous flow (micro-)reactors for heterogeneously catalyzed reactions: Main design and modelling issues

Ilenia Rossetti

Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit Milano-Università, via C. Golgi 19, 20133 Milano, Italy

ARTICLE INFO

Keywords:
Flow chemistry
Microreactors
Multiphase reactors
Heterogeneously catalysed reactions
Process intensification
Heat and mass transfer
CFD modelling

ABSTRACT

Continuous flow chemistry is a rapidly developing branch in organic and drugs synthesis, whereas it is common practice in heterogeneous catalysis for base chemicals production. Heterogeneously catalysed synthetic protocols are being developed and can take advantage of the reaction and reactor engineering experience at the macro-scale, provided that suitable models are applied to the micro- and meso-reactors in use. The main process parameters that define possible mass, heat and momentum transport limitations in heterogeneous catalytic reactors are reviewed. Specific models applying such concepts to microreactors are proposed. Finally, examples are reported of heterogeneously catalysed reactions carried out in microreactors for different applications.

1. Introduction

Reactions in continuous mode constitute a well consolidated approach when dealing with heterogeneous catalysis in the petrochemical/refinery/energy field. By contrast, fine chemicals and, more in general, organic synthesis, typically rely on a batch reaction mode. However, in the recent past, continuous flow synthesis raised the attention also in the drug and fine chemicals synthesis, especially thanks to the development of meso- and micro-reactors. The latter are increasingly available as modules with different sizes and complexity, which have been scaled up or numbered up to an industrially relevant scale. Many very interesting reviews cover widely different applications and reaction classes, such as [1–9].

The advantages of continuous flow organic synthesis are very broad and vary from selectivity or yield improvement to safety issues. Batch processes are advantageous due to their versatility, flexibility and traceability, but scale up is sometimes hard when important heat and mass transfer issues may severely limit productivity, selectivity or safety.

Continuous processes are often more efficient and demand lower manpower due to highly automatized procedures. Furthermore, they are typically characterised by lower costs, reduced wastes, with an improved environmental footprint, decreased time-to-market for new drugs and products [10,11].

Safety improvement is also widely reported. Due to the small size and very efficient and fast mixing, transport limitations are limited with respect to batch reactors. Therefore, very fast and exothermal reactions can be better carried out in microreactors in a much more controlled way. Intrinsically safer conditions are also guaranteed by the very small reactants/intermediates amount circulating in the system. This broadens the choice of reactions to give the desired product or intermediate to options that would not be selected in a bigger apparatus due to toxicity, instability, etc. Sometimes those options may lead to improved yield or lower environmental impact than conventional routes.

Improved mass transfer brings about advantages also from the point of view of selectivity and yield [12].

Very comprehensive reviews have been published, which include numerous examples of organic reactions in continuous mode. However, some asynchrony has been recently evidenced in this field [7,13]. On one hand, there is an explosive interest on continuous flow synthesis using micro- or meso-reactors, with focus on the synthetic details. On the other hand, only in some, very inspiring cases, the chemical reaction engineering, reactor engineering and transport phenomena issues are taken into account. This mismatch seems critical for scale up, optimisation and technology transfer.

When heterogeneous catalytic reactions are taken into account additional criticisms arise, because heat, mass and momentum transfer can play a predominant role and all these features should be correctly tackled for proper reactor and industrial process sizing. Additionally, while industrial catalytic packed bed reactors can take advantage of a known dependence of performance on size and shaping of the catalyst particles, in microreactors porous monoliths or powdered beds are used, which introduce new problems when defining fluid dynamics and transport phenomena.

More in general, a cultural mismatch seems evident. When micro or

E-mail address: ilenia.rossetti@unimi.it.

http://dx.doi.org/10.1016/j.cattod.2017.09.040
Received 1 August 2017; Received in revised form 6 September 2017; Accepted 21 September 2017

mesoreactors are used for base chemicals production, for environmental remediation or in the energy field, the typical concepts of industrial heterogeneous catalysis (*e.g.* heat transport across the catalytic bed, pressure drop estimation, intra- and extra-particle mass transfer issues) are appropriately transferred to the desired scale. In many cases, specific correlations are used or developed to estimate the required parameters, as will be exemplified in the following. On the contrary, when heterogeneous catalysis is applied with success to drugs, intermediates or fine chemicals synthesis, these points are often missing, leading to a description which is mainly phenomenological, thus limiting technology transfer or scale up possibilities to experimental optimisation. Thus, the study from a chemical engineering point of view of all these new reacting systems should be tackled carefully, opening a very promising, multidisciplinary field of study. The topic is further complicated by the fact that multiphase systems are intrinsically present (gas/solid, liquid/solid and even gas/liquid/solid) and that the catalytic action can take place only after adsorption of the reactants and includes safe desorption of products on/from the active sites over catalyst surface. Hence, appropriate mass transfer and kinetic models have to be applied.

On this basis, this review points out some engineering milestones that should be considered during the design of heterogenerously catalysed organic synthesis in continuous mode. Particular attention will be focused on modelling the relevant transport phenomena and catalytic (micro-/meso-)reactors. Applicative examples will be discussed across the text.

2. Heterogeneous catalytic microreactors

Heterogeneous catalytic reactors can be classified into three main types: i) packed bed, ii) wall coated and iii) micro-monolithic [14] (Fig. 1).

They can usefully find application in the case of very slow or very fast kinetics. For instance, Grignard reactions can generate a very intense hot spot which limits the yield, besides inducing safety issues. The efficient heat transfer and the possibility to design multi-injection systems lead to better temperature control in microreactors. Intrinsically safer operation is also guaranteed, such as in the case of acetone cyanohydrin synthesis, used as source of HCN [15].

Packed bed microreactors are among the most used, due to easy assembly, high possible catalyst loading. Nevertheless, heat and mass transport limitations can easily occur and significant pressure drop can arise [14,16].

Preliminary calculations, paying attention to transport phenomena, can be used in order to ensure the operability of the reactors. Appropriate description of mixing, residence time distribution and heat/mass transfer is needed for scale up and optimisation. Plug flow behaviour and short mixing times could be confirmed for all investigated flow reactors. Furthermore, interactions of reaction kinetics and the formation of hot spots in the reactor channel should be investigated.

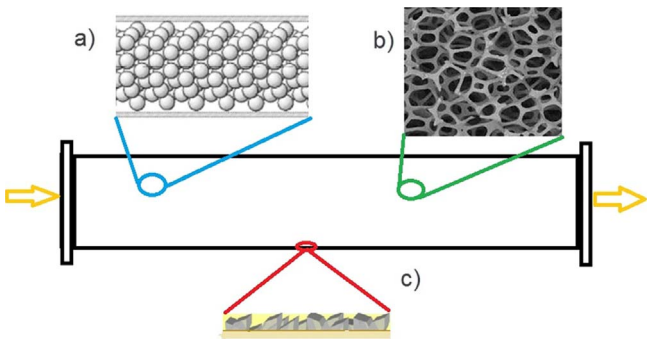

Fig. 1. Classification of heterogeneously catalysed microreactors: a) fixed bed; b) micromonoliths; c) wall coated microchannels.

2.1. Modelling transport phenomena in heterogeneous catalytic reactors

2.1.1. Mass transfer

Mass and heat transfer must be computed at the surface and in the catalyst particle. In microreactors, the reduction of size can modify the transport rate, and thus its effect on the apparent kinetics has to be checked. An additional question also arises, whether the correlations developed for classic reactors are also applicable to microreactors.

Mass transport includes the diffusion of the reactants/products across the surface layer of fluid around the catalyst particle, as well as, through the porous network of the catalyst. The former is called external or extra-particle diffusion, the latter internal or intra-particle.

2.1.1.1. External mass transfer. External mass transport rate is proportional to the difference between the reactant concentration in the bulk of the fluid and on the surface of the catalyst particle (more in general on the interphase).

$$N_A = k_g(C_A - C_{As}) \tag{E1}$$

where N_A is the molar flowrate of reactant A (kmol/m^2 s), k_g is the mass transfer coefficient and C_A/C_{As} are reactant concentrations in the bulk of the fluid and on catalyst particle surface.

The reaction rate depends on the concentration of the reactant available on catalyst surface sites, so that, under steady state conditions, the reaction is either limited by the reaction rate itself, or by the reactant refill rate to the surface (e.g. at high temperature or with anyway fast reactions). The two resistances can be considered in series to give the following equation in the simpler first order reactions case:

$$r_A = \left(\frac{1}{k_g} + \frac{1}{k_r}\right)^{-1} C_A \tag{E2}$$

where r_A is the observed reaction rate and k_r the intrinsic kinetic constant (for 1st order reactions).

Two dimensionless numbers are defined to account for the effect of external mass transport, the first (Da_I) and second (Da_{II}) Damköhler numbers:

$$Da_I = k_r C_0^{n-1}\tau \tag{E3}$$

$$Da_{II} = \frac{k_r C_0^{n-1}}{k_g S_a} \tag{E4}$$

where C_0 is the initial concentration, n is the reaction order, τ the contact time and S_a the specific surface area. Dimensionless numbers are useful to define correlations between the characteristic parameters that define a certain phenomenon, which depends on many variables. Grouping them into dimensionless groups allows to decrease the number of independent correlations to be established among parameters. Furthermore, the correlations are typically independent from the size of the system. This is a huge advantage, since it allows to derive models on a small scale, to be applied to a full scale plant. The approach is powerful and it is based on different methods that allow the determination of the number and the form of the groups that fully describe the system. The correlation between the dimensionless groups is derived from the fit of experimental data. However, caution is needed in the selection of the model, because its mathematical form is based on the correlation of data, thus it is strictly valid only in the range of values used during the experimentation. Extrapolation outside these limits is particularly not recommended.

In this specific case, Da_I is useful for appropriate calculation of kinetic parameters, which are determined within 10% error due to external mass transfer limitations if $Da_I < 0.1$. By contrast, Da_{II} compares the numerator, which depends on reaction rate, with the transport rate at denominator. High values of Da_{II} denote a reaction which is limited by external mass transfer.

k_g can be calculated from the experimental correlation of