

Modelling of the Temporal Analysis of Products (TAP) Reactor with COMSOL

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Abstract: TAP reactor is a fixed-bed catalytic reactor operated in pulse (transient) mode under very low pressures ("evacuated pulse micro-reactor"). It has become a very important tool in catalytic studies as it fills the material and pressure gaps existing between practical conditions and high vacuum – monocrystal techniques. A conveniently pretreated solid catalyst maintained at a desired temperature T in an evacuated chamber is exposed to a series of very narrow gas pulses (width < 1 ms) containing generally reactants of the studied reaction and an inert gas, as internal standard. The molecules leaving the reactor are analyzed by mass spectroscopy (MS). The obtained curves are analyzed to obtain qualitative and quantitative information about catalytic reactions.

COMSOL provides an easy way to modelize TAP results, particularly when dealing with non-standard experiments. COMSOL models can be converted to scripts (m-files) and used as central parts of optimization programs for the determination of relevant kinetic constants.

Keywords: catalysis, chemical kinetics, TAP reactor

1. Introduction

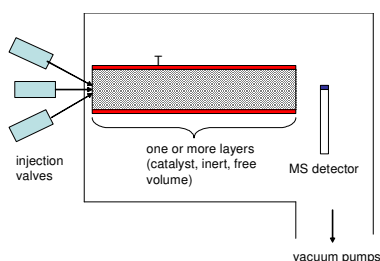


Figure 1. Schema of a TAP reactor

TAP (Transient Analysis of Products) reactor, Fig. 1, is a special catalytic reactor

operated under transient conditions in which a continuously evacuated bed of solid catalyst is exposed to narrow (microsecond) pulses of gases[1-4].

The molecules leaving the bed are analyzed at a very high rate by mass spectrometry (usually one ionic mass at a time). Such an apparatus allows performing many experiments important for understanding the ways the catalyst acts and for improvement its performances. In particular, by analyzing the experimental curves the values of the reaction rates, kinetic constants etc. can be determined. To achieve this, the systems of differential equations governing the pertinent processes must be solved. In the simplest cases, when the geometry of the reactor can be reduced to 1D case (x):

$$\varepsilon_b \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + R \quad (1)$$

where c = concentration of given molecules in the gas phase, D = their effective diffusivity, ε_b = bed porosity, and R = source (usually associated with chemical reactions). The term representing convection is omitted, since the reactor is (should be) operated in the Knudsen regime (very low pressures, even during the passing of pulses), for which the flow of gas can be entirely associated with the diffusion process.

A very special advantage of the TAP reactor is its operating in the Knudsen regime, because in this regime the diffusivities of different molecules are independent on gas composition and on pressure, and their values vary with temperature and gas nature in a very simple way:

$$D_i(T) = D_j(T_0) \sqrt{\frac{TM_j}{T_0 M_i}} \quad (2)$$

where M_i = molar mass of a substance (gas) “i”.

The actual TAP reactor contains usually three successive layers: inert 1, catalyst, inert 2, with a small void volume between the injection valves and inert 1. The details of the construction of existing TAP and TAP-like reactors are given in the literature. Their main advantage is the possibility of studying practical catalysts under the conditions approaching those of monocrystal-molecular beams experiments. Main drawback, besides the high vacuum conditions and high cost, is the necessity to use sophisticated mathematical treatment to extract the kinetic information.

2. TAP experiments

As already explained, TAP experiments consist in introduced pulses of typically 10^{15} molecules on a conveniently pretreated and evacuated catalyst. The pulses contain an inert (noble) gas and one or more active gases. The sufficiently small size of the pulses should impose the Knudsen regime in the reactor, and on the other hand ascertain that the ratio of the amount of active molecules to that of the active sites at the catalyst surface is very low ($10^{-4} - 10^{-3}$). This means that the amount (and coverage) of free active sites can be taken as constant. This allows using whole sequences of identical pulses to be employed (10 – 1000), and the results averaged to improve the signal-to-noise ratio. Such experiments are called “single-pulse experiments” (SP), whatever the number of identical pulses in one train, as long as the above condition holds for the whole sequence.

When the number of identical pulses is so high that the total number of active molecules becomes much higher than the number of active sites present, the catalyst is modified (e.g. reduced or oxidized) and the corresponding experiment becomes “multiple-pulse experiment” (MP).

Finally, alternant pulses containing different active substances may be used, to study the life span of active intermediates at the catalyst surface; these are called “alternating pulse” (AP) or “pulse-probe” experiments. A pulse of a reactant generating the intermediates is applied as first (“pump pulse”), and a pulse of another gas reacting with these intermediates is applied after some (variable) time interval (“probe

pulse”). The formation of the product is followed as usual by MS.

The modelling of SP experiments has been treated extensively in the literature, and various approximations discussed; the existing methods can be divided into analytical and numerical ones. In the first case, the PDE system is solved using Laplace transformation, and the initial pulse is represented generally as Dirac δ -function. This approach is limited to systems with linear terms in the reaction part of the equation.

The numerical methods, while more time-consuming, are not subject to this limitation; they can use more realistic representations of the pulses. Most utilized methods linearize the variations of the concentrations with “x” in the reactor (method of knots).

While the ready packages exist which treat adequately typical situations, a flexible and user-friendly programming tool like Comsol can be advantageously used to treat nonstandard experiments, compare various hypotheses concerning the validity of approximations used, etc. Created to treat problems involving systems of partial differential equations, Comsol is well adapted to model different versions of TAP experiments, and a conversion of model files to scripts (m-files) allows their incorporation into typical optimizing programs (e.g. in Matlab) to determine the parameters of these models, diffusion coefficients and kinetic constants.

In the following, some Comsol models of TAP experiments will be discussed, beginning with the simplest case, one-zone reactor filled with a nonporous solid, subjected to pulses of an inert gas.

3. Examples of Comsol modeling of TAP experiments

3.1. One-zone Reactor, non porous inert solid

The simplest case is represented by the 1-zone reactor filled only with one nonporous solid. Since the radial dispersion can be generally neglected, and the gas flow in the reactor is governed by the laws of the Knudsen domain, the modeling can be achieved by selecting 1D model, Diffusion, Time dependent (Chemical Engineering Module).

The geometry of the reactor is represented by a linear section of a length equal to that of the

solid bed (L), and the coefficients of the Comsol equation:

$$\delta_{ts} \frac{\partial c}{\partial t} + \nabla(-D\nabla c) = R \quad (3)$$

can be chosen as follows: $\delta_{ts} = \varepsilon_b$, $D = D_{\text{Knudsen}}$, and $R = r\rho_b$ (c in mol/m^3 , r in $\text{mol}/(\text{s kg}_{\text{cat}})$, ρ_b in kg/m^3). The boundary conditions are Flow, at the inlet, and Concentration, for the outlet of the reactor. The concentration is taken as zero, because the reactor outlet is continuously evacuated. The signal of Mass Spectrometer is considered as proportional to the Flow at $x = L$.

Such experiments are mostly used to determine the efficient Knudsen diffusivities of inert gas in the inert solid, so $R = 0$.

In this work the following expression for the pulse will be mostly used:

$$F_i = F_i^\circ t/\tau^2 \exp(-t/\tau) \quad (4)$$

F_i° being $N_i/(N_A A)$, with N_i = number of molecules “i” in a pulse, N_A = number of Avogadro, A = area of the reactor. The temporal part of (3) is normalized, so the integral of “F” between 0 and ∞ is equal to F_i° . The maximum of F_i is at $t = \tau$, its full width at half-height is about 2.32τ .

This case is important because it can be treated analytically, using Laplace transform of the equation (1); with initial pulse taken as Dirac δ function:

$$\frac{F}{N} = \frac{D\pi}{\varepsilon_b L^2} \sum_{n=0}^{\infty} (-1)^n (2n+1) * \exp\left(- (n+0.5)^2 \pi^2 \frac{tD}{\varepsilon_b L^2}\right) \quad (5)$$

F is the flow at the outlet of the reactor ($x = L$). Fig. 2 compares the results obtained from equation (5) and those produced by a COMSOL model, for argon in a bed of inert ($L = 0.02$ m, inner diameter $d = 0.005$ m, $\varepsilon_b = 0.5$, $D = 0.003$ m^2/s), and the Comsol model curves for two values of τ . To produce figure 2, the Comsol model was saved as a m-file and completed by a Matlab computation of F from eq. (5). A very good agreement is obvious if $\tau \leq 10^{-4}$ s. The “true” value of τ depends on the TAP apparatus used, so the precision of the approximation $F = F^\circ \delta(t)$ is not obvious.

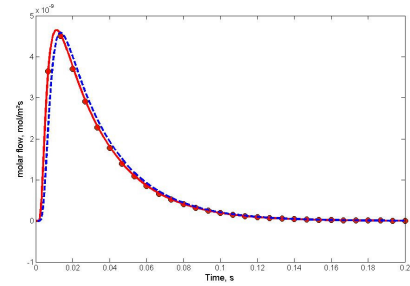


Figure 2. Diffusion in a 1-zone TAP reactor. Points computed from equation (5), continuous curves: Comsol model for $\tau = 10^{-4}$ s (continuous line) and for $\tau = 10^{-3}$ s (dashed line). Further details in the text.

It should be stressed, however, that the time necessary to compute the Comsol curve is much longer than for the analytical solution.

3.2. Alternating Pulses (“Pump-Probe”) Experiments in a One-Zone Reactor (1D)

As already indicated, in alternating pulse experiments a pulse of a reactant generating the intermediates is applied as first (“pump pulse”), and a pulse of another gas reacting with these intermediates (“probe pulse”) is applied after some interval of time.

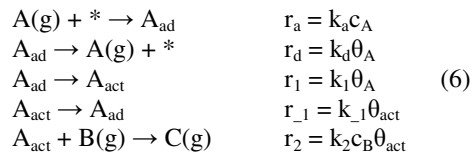
To our knowledge, such experiments were interpreted always by inspection, without modelling. However, it may be interesting to model such experiments, and Comsol may be used to that effect.

The following will be based on published results on the oxidation of carbon monoxide with oxygen on gold catalysts [5, 6].

The reactor with inner diameter $d_r = 2$ mm contains a 10 mm layer of the catalyst, preceded by a void space of 1 mm. The bed density ρ_b is equal to 3000 kg/m^3 , and the active sites concentration $n_s = 0.01$ mol/kg .

The catalyst is exposed to pump pulses of reactant “A”, each followed after a laps of time Δt by a probe pulse of reactant “B”, at a temperature of 423 K.

The mechanism of reaction is supposed to be



“ r_i ” are the rates of corresponding reaction steps, in s^{-1} (moles transformed per mole of active sites per second; “turnover numbers”) “*” are free active sites, θ_i is the coverage of active sites by adsorbed species “i” (proportion of the active sites occupied by species “i”).

Species A from the gas phase adsorbs reversibly on free active sites (their coverage, θ_* is considered as equal to 1 and omitted), and the initial adsorbed species A_{ad} are transformed reversibly to active species A_{act} which may react irreversibly with species B from the gas phase giving directly gas phase product C.

Pump pulse was considered as represented by eq. (4) with $\tau = 10^{-3}$ s; for the probe pulse a Gaussian expression

$$F = F^\circ / (\sigma\sqrt{\pi}) \exp(-(t-\Delta t)^2/\sigma^2) \quad (4a)$$

with the same full width at half-height was selected, because of the numerical stability of the model. The number of molecules in both pulses was equal to 10^{15} . The molar masses of gas-phase species were taken as $M_A = 32$, $M_B = 28$ and $M_C = 44$.

In the Navigator, 1D geometry is selected, Chemical Engineering Module, Diffusion, Time-dependent, with dependent variables ca, cb, cc, sa, sact (for c_A , c_B , c_C , θ_A and θ_{act} , respectively).

The model has two subdomains, void space and catalyst bed. For the first one $\delta_{is} = 1$, and D_i for gas species A, B and C are given by Knudsen equation for diffusivities in a circular canal with a diameter d :

$$D_i = \frac{2d}{3} \sqrt{\frac{RT}{\pi M_i}} \quad (5)$$

(it is usual to treat such void sections as CSTR; in Comsol it is easier to use the approach applied here, probably more adequate). D_i for adsorbed species in both subdomains are taken as 0. Reaction terms R are obviously omitted.

For the catalyst bed, as in the previously considered case, $\delta_{is} = \epsilon_b = 0.23$, D_i for gas species (variables ca, cb, cc) are given by eq. (2) with $M^\circ = 40$, $T^\circ = 423$ K and $D^\circ = 1.41 \cdot 10^{-5}$ m^2/s . Reaction terms can be deduced from equations (6):

$$\begin{aligned} \text{ca:} \quad & R = (-r_a + r_d) * n_s * \rho_b \\ \text{cb:} \quad & R = -r_2 * n_s * \rho_b \\ \text{cc:} \quad & R = r_2 * n_s * \rho_b \\ \text{sa:} \quad & R = r_a - r_d - r_1 + r_{-1} \\ \text{sact:} \quad & R = r_1 - r_{-1} - r_2 \end{aligned} \quad (6)$$

Boundary conditions for the inlet are Flow for ca, cb and cc: FA and FB given by eq. (4) and (4a) respectively, and FC = 0, Insulation/Symmetry for sa and sact. At the outlet of reactor, Boundary condition are Concentration, $c = 0$ for all gas phase species, and Insulation/Symmetry for adsorbed species. The results obtained with rate constants of eq. (6): $k_a = 0.005$ $m^3/(mol s)$, $k_d = 0.1$ s^{-1} , $k_1 = k_{-1} = 10$ and $k_2 = 1000$ $m^3/(mol s)$ are presented in figure 3.

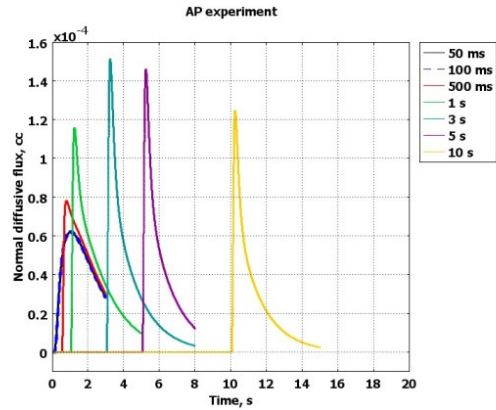


Figure 3. Modelling of an AP experiment. Pump pulse (A) at time $t = 0$, Probe pulse (B) at $t = \Delta t$ indicated. The curves represent flow of the product (C) at $x = L$. Further details given in the text.

These curves are markedly similar to experimental curves obtained in TAP experiments for the reaction



on a $Au/Ti(OH)_4$ catalyst (Figure 4).

A better agreement could be achieved with optimized kinetic constants.

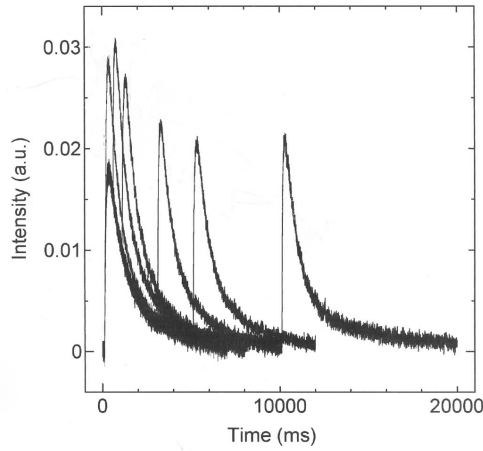


Figure 4. Experimental AP curves (CO₂ signal); oxygen pulse at $t = 0$, carbon monoxide pulse at $t=0.05, 0.1, 0.5, 1, 3, 5$ and 10 s

3.3. Diffusion and irreversible adsorption in a porous catalyst; 3-zone reactor

When a catalytic reaction is taking place on a porous catalyst, transport phenomena can influence the observed results. This is true for the TAP reactor, too. A simplified analysis of this influence may be performed by means of Comsol; the following treatment is based on the paper by Phanawadee et al. [7].

Let's consider a 3-zone TAP reactor with a void zone of 1.0 mm, first inert zone of 3.37 mm, catalyst layer of 13.85 mm, and the second inert zone of 13.54 mm. Mean size of catalyst particles $D_{\text{pellet}} = 0.4$ mm, bed density ρ_b is 400 kg/m³ and the concentration of active sites n_s is 0.08 mol/kg. The porosity of the inert bed (non porous solid) and of the intergranular porosity of the catalyst are equal to $\epsilon_b = 0.5$, the porosity of the grains of the catalyst (intragranular porosity) is $\epsilon_p = 0.4$. The reactor diameter is equal to 5 mm.

When the influence of the mass transfer in the pores of the catalyst is not considered explicitly, the reactor can be modelled as composed of 4 zones, with following settings: In the Model Navigator: 1D, Chemical Engineering Module, Diffusion, Time-dependent; dependent variable "c". Geometry corresponds to the description above (see Figure 5a).

Physics: subdomain 1 (void volume): $\delta_{st} = 1$, $D = D_{\text{Knudsen}}$ (equation 5), $R = 0$, subdomain 2 and 4 (inert 1 and 2, respectively): $\delta_{st} = \epsilon = 0.5$, $D = D_{\text{effective}}$ (equation 2), $R = 0$, subdomain 3 (catalyst): $\delta_{st} = \epsilon_b = 0.5$, or ϵ_t , $\epsilon_t = \epsilon_b + (1 - \epsilon_b)\epsilon_p = 0.7$. ϵ_t is total porosity of the catalyst layer; the first case correspond to the complete exclusion of the intragranular porosity, the second one, to its total participation [8] $D = D_{\text{effective}}$, $R = r \cdot n_s \cdot \rho_b$, where r is reaction rate in s⁻¹.

Boundary settings can be taken as before, Flux (equation 4) at the inlet, Concentration ($c = 0$) for the outlet.

To take into account diffusion and reaction in the pores, the reactor will be modelled using two geometries, one 1D, identical with the previously detailed, for the intergranular diffusion in all zones of the reactor (dependent variable c), the other one, 2D, for the diffusion in the pores (c_1). In both geometries, the physics corresponds to time-dependent diffusion (chdi).

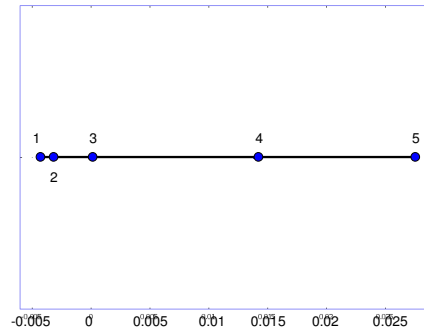


Figure 5a. Geometry 1

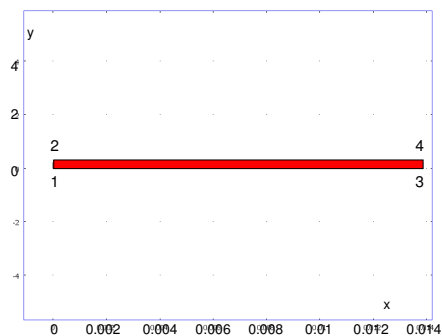


Figure 5b. Geometry 2

The coupling between the two geometries is realized by means of two extrusion coupling variables: concentration at the openings of pores $c1(y=0)$ is equal to the local concentration c , and the source term in the catalyst layer, Geometry 1 is related to the gradient of $c1$ at $y = 0$.

In Geometry 1, subdomain and boundary settings are as before, with the exception of the source term R:

$$R = \frac{(1 - \varepsilon_b) \varepsilon_p}{D_{\text{pellet}}/2} D_p \left(\frac{\partial c1}{\partial y} \right)_{y=0} \quad (6)$$

(active sites on the external surface are neglected [7]), where D_p , effective diffusion coefficient in the pores, has been estimated as [7]:

$$D_p = D_b \frac{\varepsilon_p (1 - \varepsilon_b) \overline{d_{\text{pore}}}}{2 \varepsilon_b^2 D_{\text{pellet}}} \quad (7)$$

$\overline{d_{\text{pore}}}$ = mean pore diameter.

In Geometry 2, the unique subdomain is a rectangle, with one boundary (width, $y = 0$) corresponding to the catalyst bed in Geometry 1, and height equal to $D_{\text{pellet}}/2$.

Subdomain settings are as follows: $\delta_{\text{ts}} = \varepsilon_p$, $R = r * n_s * p_b$; diffusion coefficient is anisotropic, axisymmetric:

$$D = \begin{bmatrix} 0 & 0 \\ 0 & D_p \end{bmatrix}$$

(the pores are considered as not connected).

For the boundaries, the settings are Concentration, $c1 = c10$ for the boundary lying on $y = 0$ axis, and Insulation/Symmetry for the others.

The coupling extrusion variables are introduced as follows. In Geometry 1, Subdomain 3 variable, $c10$ (Geometry 2) = c , source vertices 3, 4, destination vertices 1, 3. In Geometry 2, Boundary 2, gr (Geometry 1) = $c1y$, source vertices 1, 3 destination vertices 3, 4 ($gr = \partial c1 / \partial y$, see eq. (6)).

The results: flow at outlet of the reactor, Geometry 1, obtained for various pore diameters are presented in Fig. 6 (diffusion only, $r = 0$), and compared with two extreme cases discussed

before (pores totally excluded or totally participating). Other parameters: $\varepsilon_b = 0.5$, $\varepsilon_p = 0.4$, $D_b(\text{inert}) = 0.003 \text{ m}^2/\text{s}$, $D_b(\text{catalyst}) = 0.002 \text{ m}^2/\text{s}$. It is evident, that for a particle size as high as 0.4 mm, the participation of pores is quite limited, even for pores as large as 200 nm.

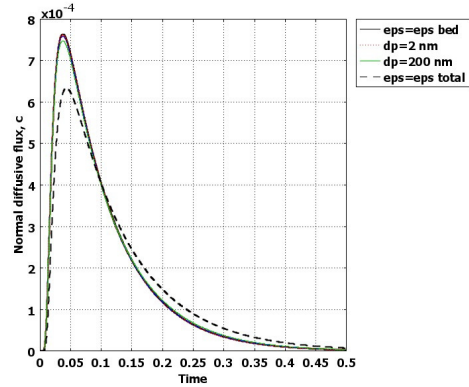


Figure 6. Influence of the pore size on the diffusion in a TAP reactor; mean particle size 0.4 mm.

4. Conclusions

Comsol provides interesting possibilities in modeling of TAP experiments. Its big advantages are user-friendly GUI interface to deal with standard problems, and many more sophisticated tools to model less standard aspects (coupling function, PDE programming, etc.). Problems including nonlinear terms can be treated without difficulty. Another advantage is the possibility of including e.g. heat transfer aspects by means of “multiphysics” approach. The obtained results can be easily represented in various types of figures, and the Comsol model can be easily converted to m-files and incorporated in bigger Matlab programs to further treat the results of modeling, e.g. to estimate the constants (diffusivities, rate constants).

Disadvantages of such approach are longer computation times in comparison with analytical methods, when they are available, and the necessity to avoid discontinuities and singularities in the problems. However, such discontinuities do not represent adequately real experimental conditions. Since the pulses used in TAP experiments are very narrow, some care must be taken when choosing the steps of time and mode of timestepping (‘strict’ or ‘intermediate’ instead of ‘free’, when necessary).

Treatment of big models may encounter 'out of memory' problems or very long times of execution.

5. References

1. Gleaves, J.T., J.R. Ebner, and T.C. Kuechler, Temporal analysis of products (TAP) - a unique catalyst evaluation system with submillisecond time resolution, *Catalysis Reviews - Science and Engineering*, **30**, 49-116 (1988)
2. Gleaves, J.T., et al., TAP-2, An interrogative kinetics approach, *Applied Catalysis A : General*, **160**, 55-88 (1997).
3. Yablonsky, G.S., M. Olea, and G.B. Marin, Temporal analysis of products: basic principles, applications, and theory, *Journal of Catalysis*, **216**, 120-134 (2003).
4. Perez-Ramirez, J. and E.V. Kondratenko, Evolution, achievements, and perspectives of the TAP technique, *Catalysis Today*, **121**, 160-169 (2007).
5. Olea, M., et al., Temporal Analysis of Products (TAP) Study of the Adsorption of CO, O₂, and CO₂ on a Au/Ti(OH)₄* Catalyst, *Bulletin of the Chemical Society of Japan*, **74**, 255-265 (2001)
6. Olea, M., et al., TAP study on CO oxidation on a highly active Au/Ti catalyst (OH)₄*, *Physical Chemistry and Chemical Physics*, **3**, 627-631(2001)
7. Phanawadee, P., et al., Mathematical analysis of TAP models for porous catalyst, *Chemical Engineering Journal*, **115**, 51-62.(2005)
8. Huinink, J.P., J.H.B.J. Hoebink, and G.B. Marin., Pulse experiments over catalyst beds: a window of measurable reaction rate coefficients, *Canadian Journal of Chemical Engineering*, **74**, 580-585 (1996)

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