

# On the Characterization of Transient Response Curves in Heterogeneous Catalysis

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A previously published example of general characterization of transient response curves was analyzed by means of computer simulation. For this purpose, not only concentration responses but also responses of the rates of elementary reaction steps were used. Rate responses revealed that the published different types of concentration transient responses disguised very similar kinetic behaviour. Further, the path of reversible steps to the equilibrium was followed and implications for the rate-limiting step were discussed. Questionable character of general classification of transient responses was pointed out.

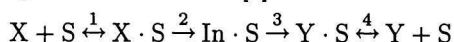
Kinetics of heterogeneous catalytic reactions is now often studied by means of nonstationary methods, the principle of which can be best found in reviews [1–3]. Many studies dealing with various particular reactions have been published. Papers concerning the general characterization of nonstationary curves are, however, rare. Studies by *Kobayashi* [4], *Salmi* [5], and *Müller* and *Hofmann* [6] are the only examples.

Although it is generally accepted that models of the stationary kinetics are not suitable for analysis of nonstationary data, results of unsteady experiments are often interpreted using the well-known concepts of stationary kinetics. For example, the rate-limiting step is sought.

Provided that values of all parameters are known, nowadays it is no problem to simulate numerically even very complex reaction mechanisms. However, only computed concentration responses are analyzed and only on this basis the conclusions on the kinetics of studied reaction are drawn. Computer modelling studies, surprisingly, do not discuss the rates of elementary reaction steps although these can be very easily computed. It is the aim of this communication to analyze some published data and conclusions [4] on the basis of true rate responses and to show how just these responses substantially improve our insights into the kinetics of a set of elementary steps.

## THEORETICAL

*Kobayashi's* mechanism [4]



of a general catalytic reaction  $X \rightarrow Y$  was chosen as an illustrative example. The reaction proceeds in a dif-

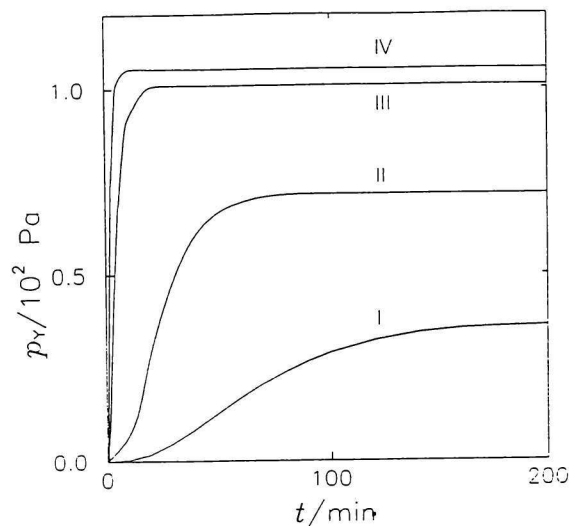


Fig. 1. Four types of transient responses of the concentration of product. Recomputed according to *Kobayashi* [4].

ferential flow reactor. All details on the mathematical model, rate constants, and values of other parameters can be found in the original paper [4].

For this mechanism the author presents, on the basis of computational modelling, four typical responses of the product (Y) partial pressure at the reactor outlet to the step increase of the input reactant (X) pressure from zero to some particular value. We have recalculated the responses and they are shown in Fig. 1, for convenience.

*Kobayashi's* conclusions are, briefly (see also Fig. 1):

1. Curves I and II exhibit an induction period (S-shape) and this means that the catalyst surface is cov-

ered with a large amount of stable intermediates.

2. Only short delay (without S-shape) exists on curve III indicating large amount of adsorbed species. This is caused by the rapid readsorption of product molecules.

3. Instantaneous response is seen on curve IV, surface coverage by the intermediates is minimal, surface reactions and product desorption are rapid, reactant adsorption is rate-limiting.

In our calculations we follow not only the concentration responses but also responses of the rates of all elementary steps and the equilibrium state of each reversible step [7]. Rates are computed from the usual law of mass action equations. For instance, the rate of the first step of Kobayashi's mechanism is expressed

$$r_1 = k_1 p_X \theta_v - k_{-1} \theta_X$$

Further, we introduced the quantity called relative distance from equilibrium [7] to describe the path to the equilibrium of reversible steps. There are two reversible steps (1 and 4) in the Kobayashi's mechanism and the corresponding quantities are defined as follows

$$D_1 = (\theta_X / p_X \theta_v) / K_X \quad D_4 = (\theta_Y / p_Y \theta_v) / K_Y$$

Obviously, in the equilibrium  $D_i = 1$ .

## RESULTS AND DISCUSSION

First of all, it should be pointed out that the shape of responses is affected by the time scale used in their graphical representation. When redrawing curve IV from the Kobayashi's scale (Fig. 1) into the more appropriate one (Fig. 2), the S-shape is revealed, which is ascribed by Kobayashi [4] only to curves I and II.

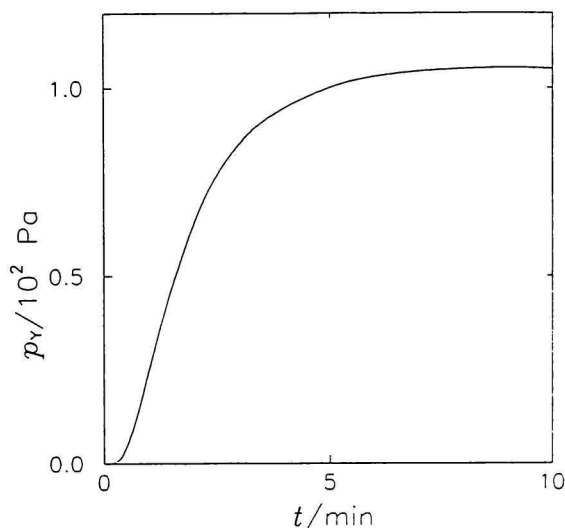


Fig. 2. Curve IV from Fig. 1 in more appropriate time coordinates.

The rate responses for Kobayashi's cases I—IV are shown in Fig. 3. Their shapes are not very different. Even the values of the rate of each corresponding elementary step are similar in all cases. The main difference consists in the width of the time interval over which are the responses spread. It is evident that all curves of the Kobayashi's classification (Fig. 1) represent the same kinetic type (kinetic behaviour) with different rates of the overall reaction process. After starting reactant feed, adsorption has always the highest rate (see Fig. 3). As the surface concentration of the reactant rises, the rate of surface reaction 2 becomes greater. This consecutively causes the increase of the rates of the remaining steps 3 and 4.

There is relatively a large amount of intermediate In on the catalyst surface in the cases I and II (cf. Kobayashi's conclusion No. 1 above):  $\theta_{In}^{ss} \approx 0.5$  (I),  $\theta_{In}^{ss} \approx 0.1$  (II). However, this is probably caused by the generally low overall reaction rate, due to the low values of the rate constants. The rate of intermediate In decomposition is namely the same as in the other cases (see Fig. 3, curves 3). Thus, intermediate In is not much more stable than in the other cases (cf. Kobayashi's conclusion No. 1).

In the case III, the rate of desorption monotonously increases and has similar value as in the other cases (see Fig. 3, curves 4). Therefore, Kobayashi's conclusion (No. 2 above) about rapid product readsorption is not valid.

Curve IV (Fig. 1) represents a very rapid overall course of reaction, although the actual values of the rates of elementary steps are similar to the other examples (see Fig. 3).

Based on all these facts, it can be further concluded that induction period (S-shape) exists on the product concentration response in any case. It is caused by delaying the step change in the reactor feed by all elementary reaction steps. The step change can be detected in the product partial pressure only after it goes through all elementary steps which precede the product formation. The more rapid are the elementary steps, the shorter is the induction period.

Case IV (Fig. 1) is said to be the example of adsorption as a rate-limiting step [4]. What does the rate-limiting step really mean in the nonsteady state? It is a mechanical application of the traditional, *i.e.* stationary concept in nonstationary kinetics. In the unsteady state, rates of all consecutive elementary steps are generally not equal. It is not simple and maybe even possible to write an expression for some overall reaction rate which should be limited by the rate-limiting step. The rate-limiting step serves also for simplification in deriving the steady-state rate equation. Such simplification is not needed for the nonstationary kinetic models. The concept of rate-limiting step can be also viewed as an attempt to describe which particular elementary step determines the response of product concentration. This problem

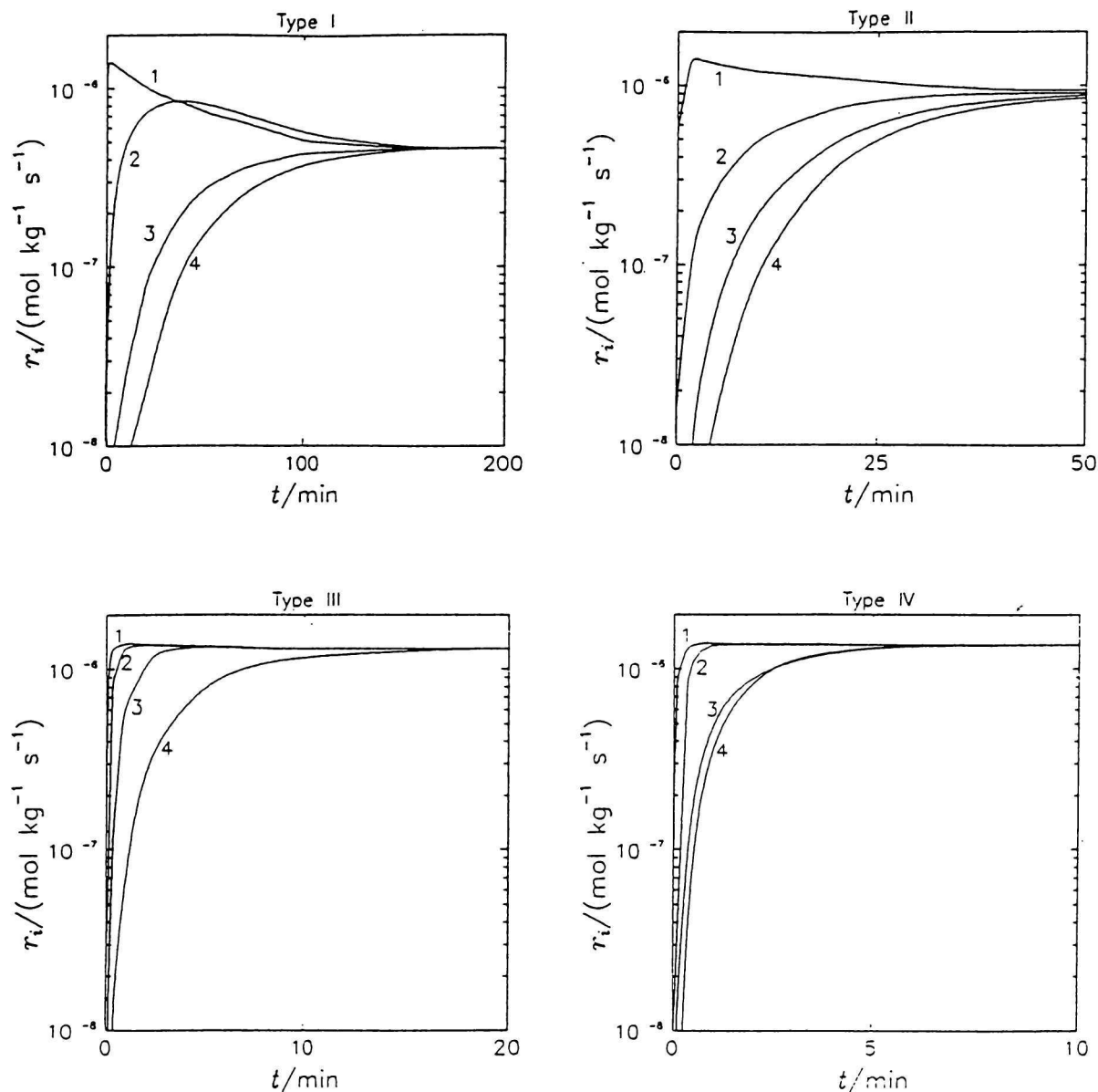


Fig. 3. Transient responses of the rates of elementary steps 1—4 for various response types (I—IV) from Fig. 1.

is addressed in another paper [7] but it can be said here that in the modelled mechanism the determining step in this sense is always the product desorption (step 4).

As it is well-known, the rate-limiting step should be far from the equilibrium in contrast to the other steps. In the Kobayashi's mechanism only the adsorption steps are reversible. Responses of their distances from equilibrium are shown in Fig. 4. In the case IV both adsorption (step 1) and desorption (step 4) are far from equilibrium, even in the steady state. Thus, both steps could be viewed as rate-limiting. In the examples II and III, desorption is soon very near the equilibrium (see Fig. 4). Adsorption then should be considered to be the rate-limiting step. However, there

are no principal differences in the curves  $r_i(t)$  between these two examples and the other two ones (see Fig. 3). Similar kinetic characteristics (Fig. 3) disguise different equilibrium behaviour (Fig. 4). From the responses of case I in Fig. 4 it is evident that the dynamics of equilibrium relations may be fairly complicated in the nonsteady state.

Calculation of  $k_1$  from the steady-state level of the  $p_Y(t)$  curve IV, shown in discussed paper [4], is possible not due to adsorption being the rate-limiting step [4] but because of low conversion and nearly free catalyst surface in the steady state. Similar calculation for the other curve III (Fig. 1) gives  $k_1 = 6.4 \times 10^{-8}$  mol/(g min kPa) which is also very close to the actual value  $6.9 \times 10^{-8}$  mol/(g min kPa) used in calculations.

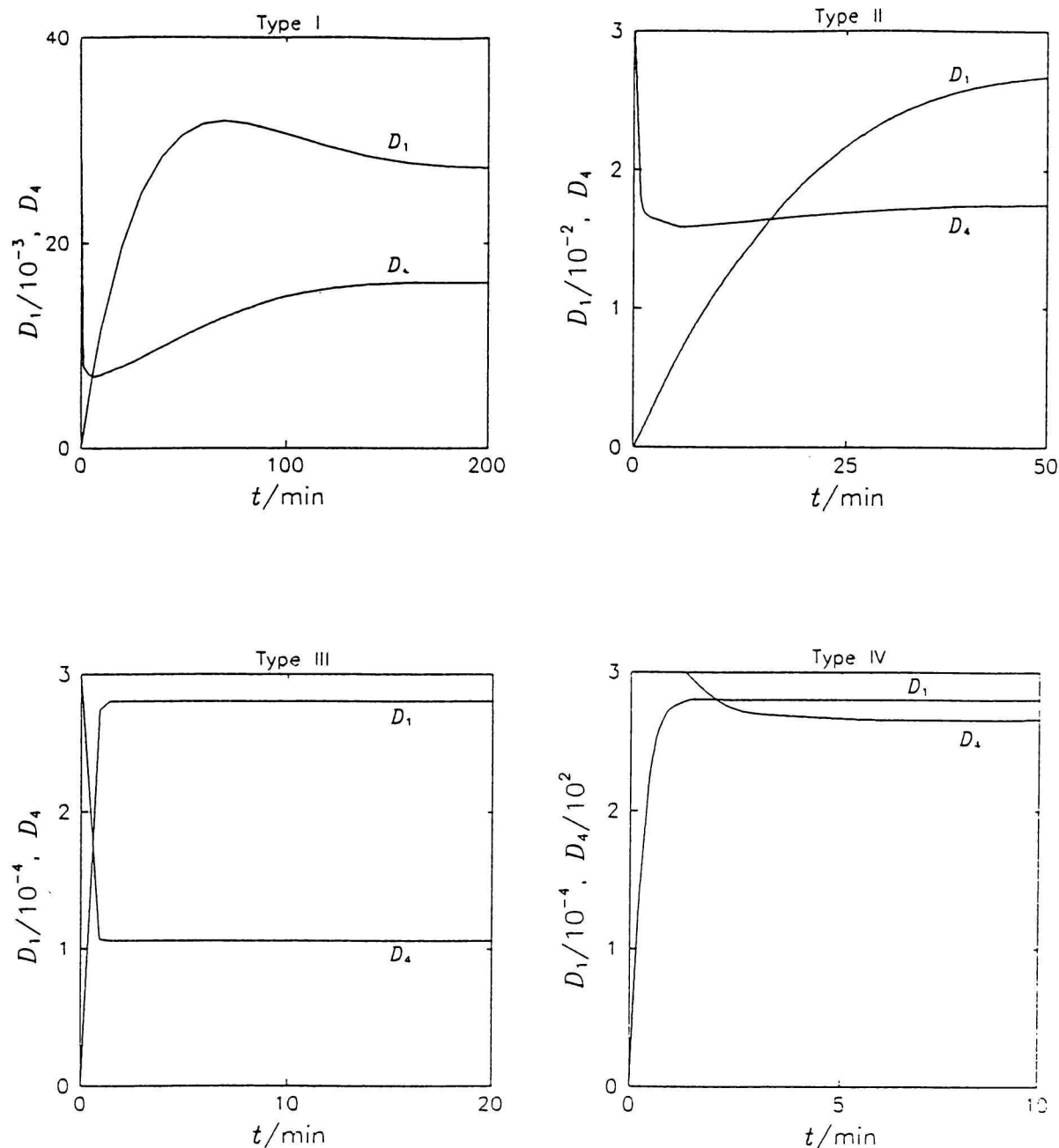


Fig. 4. Transient responses of the distances from equilibrium of elementary steps 1—4 for various response types (I—IV) from Fig. 1.

## CONCLUSION

In the computer modelling studies of nonstationary kinetics it is very fruitful to study also responses of the rates of elementary steps and the way to the equilibrium of reversible steps. More detailed information on the reaction kinetics can be thus obtained. Different shapes of measurable, *i.e.* concentration, responses may actually have very similar kinetic basis. It was also shown that similar nonstationary kinetic behaviour of various reaction systems does not nec-

essarily mean that corresponding elementary steps of these systems are in similar equilibrium state.

Kobayashi's characterization of transient response curves [4] is questionable.

## SYMBOLS

- $D_i$  relative distance from equilibrium of the  $i$ -th step
- In intermediate
- $k_i$  forward rate constant of the  $i$ -th step
- $k_{-i}$  backward rate constant of the  $i$ -th step

$K_i$	adsorption coefficient of component $i$
$p_i$	partial pressure of component $i$ at the reactor outlet
$r_i$	rate of the $i$ -th step
S	catalyst active site
$t$	time
X	reactant
Y	product
$\theta_i$	fractional surface coverage of component $i$
$\theta_v$	fractional coverage of vacant active sites
ss	(index) steady-state value

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