Transient Behavior of Heterogeneous Catalytic Reactions with Educt Inhibition

Under periodic operating conditions, the instantaneous rate of the heterogeneous catalytic addition of acetic acid to ethylene can be an order of magnitude higher than at steady state. A real surface, multistep control model takes into account the strong inhibition of the acid to ethylene sorption and describes the steady state and transient behavior quantitatively.

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SCOPE

In a number of experimental studies it was shown that the periodic change of reactant concentrations in the feed of continuous heterogeneous catalytic reactors can lead to an improvement of reactor performance. Examples have been published by Unni et al. (1973) for the catalytic oxidation of SO_2 on V_2O_5, by Cutlip (1979) for the oxidation of CO on platinum, and by Abdul-Kareem et al. (1980) for the CO oxidation on V_2O_5. One of the problems concerning the use of periodic operation on an industrial scale is the difficulty of predicting reactor behavior under the influence of forced concentration variations. Grabmüller et al. (1985) and Schädlich et al. (1983) tried to predict conversion improvements due to periodic operation. Their discussions are based on simple power law models for the chemical kinetics. Lynch (1983, 1984) chose adsorption/desorption models to describe the behavior of catalytic reactors during forced periodic operation. The problem to overcome is the development of an adequate kinetic model explaining the steady state and the dynamic behavior of the reactor. This is a rather difficult task, because kinetic models developed under steady state conditions are *a priori* not suitable for predicting the dynamics of the reactor. The discrimination of dynamic catalytic reaction models via introduction of feedback was recently proposed by Lyberatos et al. (1984). In the present paper, a more conventional method of developing a physical model will be discussed.

CONCLUSIONS AND SIGNIFICANCE

Reaction models that are valid under steady state conditions are frequently not suitable for explaining the complex processes that become important in periodic operation. This is demonstrated using three different catalytic-reaction kinetic models with increasing complexity. They are based on:

- Ideal surface, one-step control
- Ideal surface, multistep control
- Real surface, multistep control

Although each of the models is suitable to describe the steady state kinetics, only the last one can be used to predict correctly reactor performance under periodic operation. This model is based on the assumption that the rate of adsorption at a real surface falls rapidly with increasing coverage of the surface. The reason can be strong inhibition by a reactant or increasing activation energy with coverage. The model used is based on the Elovich equation and predicts an exponential decrease of the rate of adsorption with increasing coverage.

Model calculations confirm the experimentally observed increase in reactor performance under periodic operation. The time-averaged reactor performance under periodic operation can be higher than any performance under steady state conditions. The achievable reaction rate under dynamic conditions is strongly influenced by the sorption rate of the inhibitor. De-

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creasing sorption rates will lower the effect of periodic operation. For instantaneous sorption rates, the obtainable increase in performance is maximal and the optimal frequency tends to be infinite (relaxed steady state conditions). For finite sorption rates, an optimal length of period and an optimal ratio of the partial periods exist.

Introduction

Catalytic reaction rate models are normally based upon the assumption that the rate is determined by only one step in a series of supposed elementary events. This supposition often has to be abandoned when kinetic studies are carried out over a large domain of reaction parameters. Due to different dependencies of the individual steps on temperature, pressure, and concentration, the rate-limiting step may change; consequently, a region must exist where rates of sorption processes and surface reactions are of the same order of magnitude. This change is often difficult to recognize when studying only global heterogeneous reaction rates.

Reaction models based on experimental data obtained under steady state conditions are often inadequate for describing the dynamic behavior of heterogeneous catalytic reactors and for explaining the performance of catalytic reactors under periodic operation. Under nonsteady conditions, the rate-limiting steps may change with time and the surface concentrations of reactants and products may assume values different from those of steady state operation, resulting in a change of catalyst performance and product selectivity. This will be demonstrated for the example of heterogeneously catalyzed addition of acetic acid to ethylene:

$$CH_3COOH + C_2H_4 \overset{cat}{=\!=} CH_3COOC_2H_5 \qquad (1)$$

The catalyst consists of a porous silica carrier, which is impregnated with sulfuric acid as described by Leupold et al. (1978, 1979) and Dettmer and Renken (1983). The following experimental observations are made:

- Under steady state conditions the global production rate of the ethyl acetate passes through a maximum with increasing partial pressure of acetic acid.
- At stepwise addition of acetic acid and in presence of catalyst pretreated with ethylene, the rate of reaction reaches a maximum during the transient period. This maximum is several times higher than the maximum reaction rate at steady state.
- The maximum steady state productivity can be enhanced considerably by forced periodic variation of the acid concentration in the feed.

To explain the experimental findings and to describe the steady state and nonsteady state behavior of the catalyst, separate studies of the sorption and reaction phenomena of the reactants were undertaken.

Experimental

A differential reactor was chosen for the experimental determination of reaction kinetics under steady state and nonsteady conditions; the set-up is shown in Figure 1. In consequence, under the applied experimental conditions, the reverse reaction could be neglected. Tables 1 and 2 respectively list the experimental parameter ranges and the characteristics of the catalyst carrier.

A bubble column is used to ensure regular feeding and vaporization of acetic acid. The variation of acetic acid partial pressure in the gas stream is effected either by change in temperature, or by altering the flow of inert gas. The stepwise variation of reactant concentration is effected by three-way valves controlled by timers. The volumetric feed to the reactor is held constant by replacing reactants by inert gases.

The reactor consists of a vertically arranged, double-jacketed tube, with an inserted small catalyst section of 0.5–5 cm length and 1.5 cm ID. The gas is preheated in a 60 cm long fixed bed filled with PTFE beads (Truffer, 1984). PTFE was chosen as inert material to avoid acetic acid adsorption and to ensure an ideal step function at the reactor entrance. The gas stream leaving the reactor is analyzed continuously by a mass spectrometer, *M.S.*, and simultaneously by a gas chromatograph, *G.C.*, at 10 min intervals.

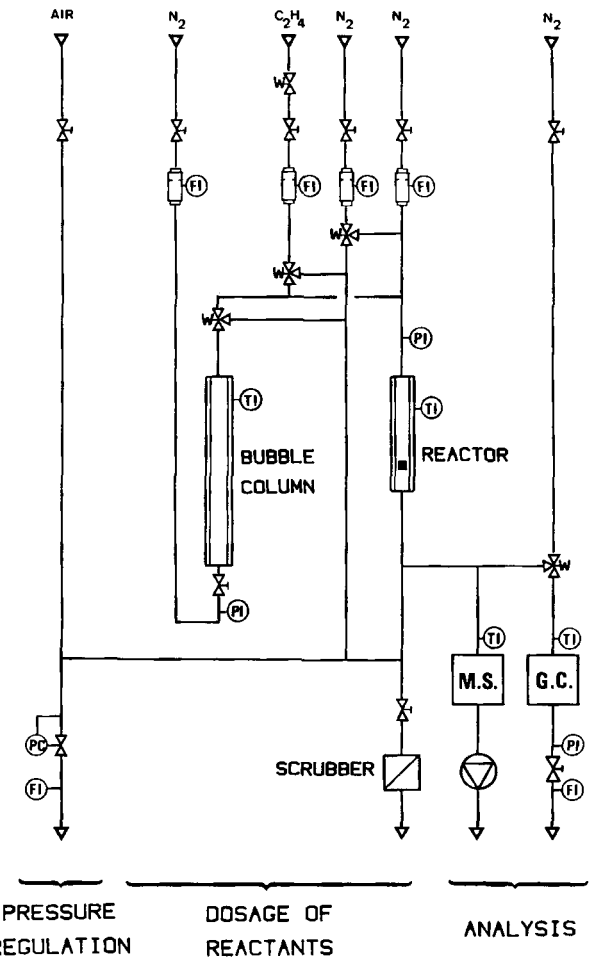

Figure 1. Flow sheet of the experimental set-up.

Table 1. Experimental Parameters

Ethylene pressure in the feed, P_{Eo}	30–135 mbar
Acid pressure in the feed, P_{Ao}	0–20 mbar
Temeprature, T	90–130°C
Feed, $\dot{V}(T_{react})$	3–15 cm³/s
Catalyst mass, m_{cat}	1–8 g

Table 2. Carrier Characteristics

Form	3 mm beads of pressed crystallites
Crystalline compound	Montmorillonite/α-quartz
Formula	$Al_2O_3 \cdot 4\,SiO_4 \cdot H_2O + \times H_2O$
Specific surface area	110–130 m²/g
Pore size distribution	1.75–0.08 μm: 0.16 cm³/g
Pore volume	80–14 mm: 0.20 cm³/g
	14–1.9 mm: 0.29 cm³/g
Apparent density	0.88 ± 0.05 g/cm³

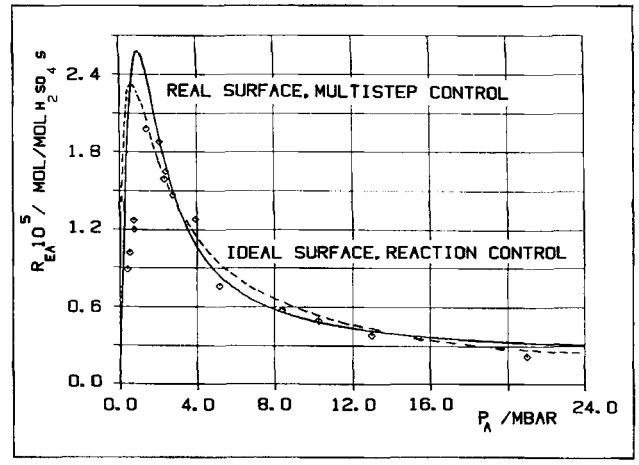

Figure 2. Reaction rate as function of the partial pressure of acetic acid.

Experimental result compared to model simulations.
T = 110°C; P = 1.05 bar; P_E = 65 mbar

Results

Under steady state conditions, the production rate of ethyl acetate is directly proportional to the partial pressure of ethylene. The influence of the gas phase concentration of acetic acid is more complex: the reaction rate increases initially with concentration, passes through a maximum, and decreases to very small values for high concentrations, Figure 2.

The transient behavior of the catalyst after a sudden change of acetic acid concentration in the feed is shown in Figure 3 and 4. For the start-up procedure, the concentration of the product and in consequence the production rate goes through a pronounced maximum within the first 40 min, depending on reaction conditions. Stationary conditions are reached after 200 to 300 min. In the experiments presented, the acetic acid feed is interrupted after 200 min. The responses at interruption are shown on the righthand side of Figure 3 and Figure 4. Depending on the reaction conditions, the rate of product formation decreases in the first 20 min, then reaches a maximum and asymptotically approaches zero. The transient time for the shutoff procedure is much longer compared to the start-up. There is still an ethyl acetate formation detectable after several hours.

The influence of ethylene concentration on the catalyst behavior is shown in Figure 3. Applying higher concentration, all extremes are slightly displaced to shorter times. At very low partial pressure of ethylene, the minimal reaction rate at the shutoff disappears. The transient period becomes shorter with higher ethylene pressures. Figure 4 shows the transient behavior for different acetic acid concentrations in the feed. As a result of the formal negative reaction order, the steady state reaction rate decreases with increasing acid concentration. Within the start-up period, the acid concentration has an opposite effect. The maximum reaction rate increases considerably with increasing

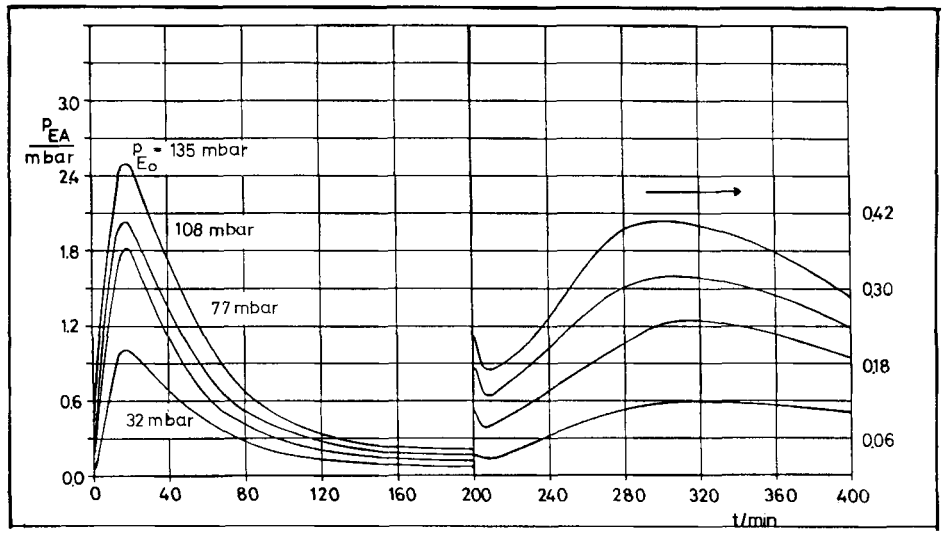

Figure 3. Measured transient behavior on stepwise variation of acetic acid feed.

Influence of ethylene pressure.
T = 100°C; P = 1.05 bar; P_{Ao} = 9 mbar

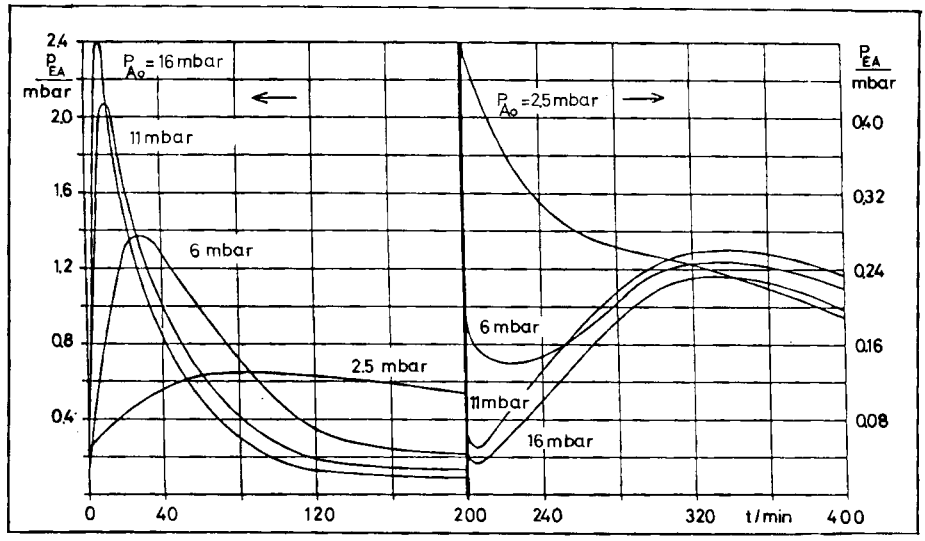

Figure 4. Measured transient behavior on stepwise variation of acetic acid feed.

Influence of acid pressure.
T = 100°C; P = 1.05 bar; P_{Eo} = 68 mbar

partial pressure of the acid. However, the decrease after the maximal value is steep and the reaction rate drops rather quickly to the small steady state performance. When the acid feed is interrupted, the transient minimal ester production is less pronounced at small acid concentration. At very small concentration, the minimum can no longer be observed.

In Figure 5, several experimental concentration-time curves are presented for different transient start-up and shutoff experiments. It is interesting to remark that the shutoff curves are completely changed when the periods are shortened. Compared to steady state kinetics, the maximal reaction rate is observed at roughly four times higher acetic acid concentration in the gas phase, indicating nonequilibrium between catalyst and gas.

Modeling

Comparison of transfer coefficients published in literature (summarized, for example, by Carberry, 1976) with the actual reaction rate shows that the influence of film and pore diffusion in the investigated range of experimental conditions is negligible. Typical values for the Damköhler number (Da II = $-R_A/k_g a C_A$) are in the order of 10^{-3} and the Weisz modulus

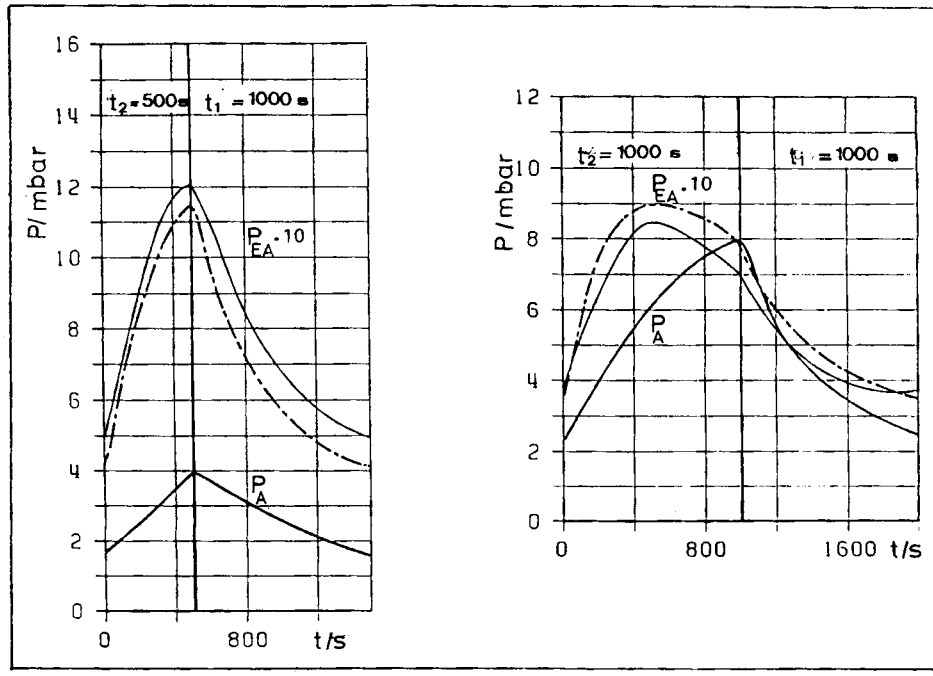

Figure 5. Measured and predicted behavior on periodic variation of acetic acid feed.

T = 110°C; P = 1.05 bar; P_{Eo} = 68 mbar

($\phi' = -R_{A,ob} \cdot r_p^2 / D^e C_A$) is found to be less than 0.02 (Dettmer, 1981). Therefore only the sorption processes and the chemical reaction are determining the observed overall reaction rate.

Ideal surface, surface-reaction control

Very simple approaches to describe catalytic reaction kinetics were proposed by Hougen and Watson (1943). Their widely used models are based upon the assumption of an ideal surface and the validity of the Langmuir adsorption isotherm. Assuming that the chemical reaction rate is the rate-limiting step, and neglecting the surface concentration of ethylene and ethylacetate, the following simple model is obtained:

$$-R_A = \frac{k_s K_E P_E \cdot K_A P_A}{(1 + K_A P_A)^2} \tag{2}$$

The two model parameters can easily be determined by curve fitting. With the numerical values of $k_s K_E = 1.3 \cdot 10^{-6}$ mol (mol $H_2SO_4 \cdot$ mbar $\cdot$ s)$^{-1}$ and $K_A = 1.3$ mbar^{-1}, the description of the experimental results is quite satisfactory, as can be seen from Figure 2. However, this simple kinetic model fails completely to describe the observed transient behavior of the catalyst. Due to the differential behavior of the small catalytic reactor, the predicted reaction rate is immediately reached. Therefore, the model cannot predict any transient behavior of the catalyst.

Multistep rate control

The previous catalytic reaction-rate model was based upon the assumption that only the chemical reaction is the rate-limiting step. Under nonsteady conditions, this assumption has to be abandoned: To reach stationary concentrations on the surface, a certain time is needed; consequently, in the first moments after a concentration change in the gas phase, the sorption rates of the reactants must have an influence on the overall transient reaction rate. The second approach to describing the steady state and nonsteady state behavior of the catalyst is therefore based upon a multistep control, assuming that sorption and surface reaction rates of the reactants i are of the same order of magnitude. The model is represented by the following set of equations:

Table 3. Model Parameters: Multistep Control, Ideal Surface

Symbols	Value	Unity
$k_{a,E}$	$6.0 \cdot 10^{-7}$	$\frac{\text{mol}}{\text{mol } H_2SO_4 \cdot \text{mbar} \cdot \text{s}}$
$k_{d,E}$	$1.6 \cdot 10^{-4}$	$\frac{1}{\text{s}}$
$k_{a,A}$	$1.2 \cdot 10^{-3}$	$\frac{1}{\text{mbar} \cdot \text{s}}$
$k_{d,A}$	$3.0 \cdot 10^{-3}$	$\frac{1}{\text{s}}$
k_s	$3.0 \cdot 10^{-3}$	$\frac{\text{mol } H_2SO_4}{\text{mol} \cdot \text{s}}$

$$R_{a,E} = k_{a,E} P_E (1 - \Sigma_i \theta_i) - k_{d,E} \theta_E \tag{3}$$

$$R_{a,A} = k_{a,A} P_A (1 - \Sigma_i \theta_i) - k_{d,A} \cdot \theta_A \tag{4}$$

$$R_{s,i} = k_s \theta_E \theta_A \tag{5}$$

The resulting model contains five parameters, Table 3, that are rather difficult to obtain by curve-fitting methods. Nevertheless, the multistep rate model predicts qualitatively the observed transient behavior of the catalyst, as can be seen in Figure 6. The high maximum of production rate after starting the acid supply is predicted, as well as the characteristic minimum and maximum of the reaction rate after stopping the acetic acid feed. But the multistep model based on ideal surface and Langmuir isotherms is unable to explain the experimentally observed increase of productivity under periodic operation (Leupold and Renken, 1978). Under the influence of periodically changed concentration, the predicted maximal reaction rate can never exceed the maximal value obtainable under optimal steady state conditions.

This is depicted in Figure 7 for different lengths of the partial periods t_1 and t_2 and different ratios of t_1/t_2. Under periodic operation, the feed concentration of acetic acid has a maximal value in the time interval t_2 and is zero within the period t_1.

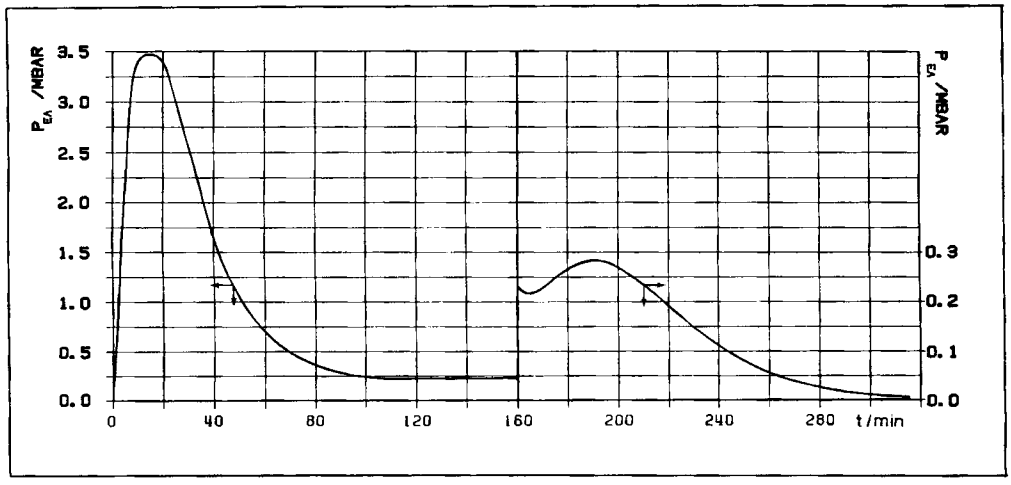

Figure 6. Simulated transient behavior on stepwise variation of acetic acid feed.
Ideal surface model, multistep control.

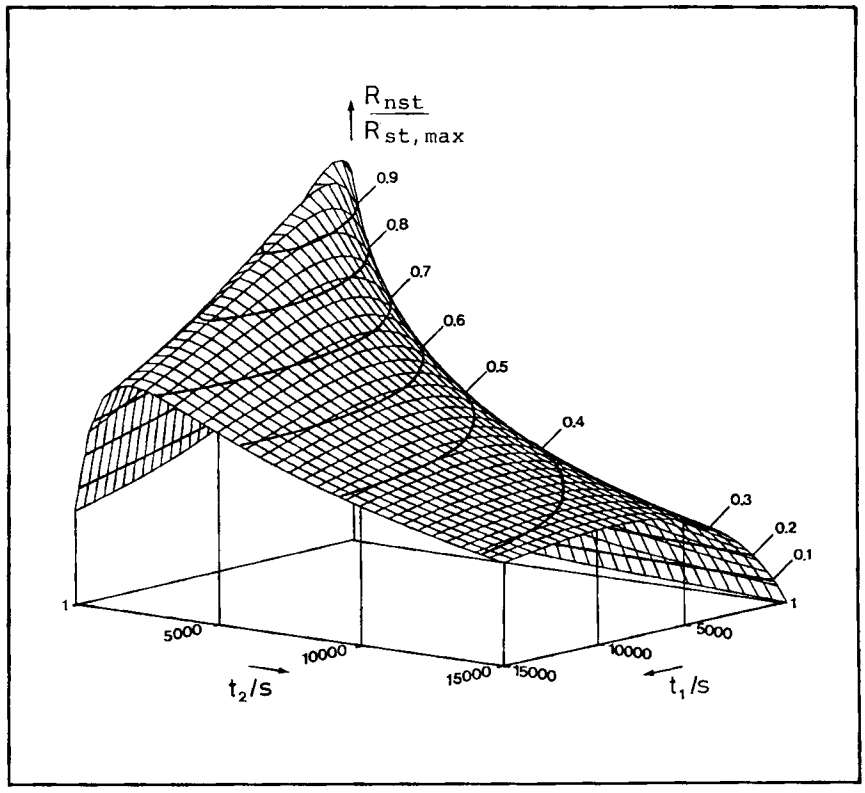

Figure 7. Predicted reactor performance at periodic operation.
Ideal surface model, multistep rate control.
P_{Ao} = 10 mbar; P_{Eo} = 68 mbar

Real surface, multistep control

At real surfaces, the adsorption and desorption rate constants may change with increasing coverage, which leads to the often observed change of the heat of adsorption. Physical reasons for this behavior can be surface heterogeneity, interaction of adsorbed species, or a combination of these. To explain the adsorption kinetics of gases on real surfaces, one can assume adsorption and desorption activation energies to be linear functions of the surface coverage θ (Carberry, 1976):

$$E_a = E_a^0 + \beta\,\theta \tag{6}$$

$$E_d = E_d^0 + \beta'\,\theta \tag{7}$$

The adsorption and desorption rate constants become:

$$k_a = k_a^0 \exp\left(-\frac{E_a^0 + \beta\,\theta}{RT}\right) \tag{8}$$

$$k_d = k_d^0 \exp\left(-\frac{E_a^0 + \beta'\,\theta}{RT}\right) \tag{9}$$

Recently Herz and Marin (1980) proposed such a model to explain experimental results for the carbon monoxide oxidation on platinum catalysts.

For high values of β and β', the influences of surface coverage in Eqs. 3 and 4 can be neglected, and one obtains the Elovich equation, used in numerous instances to describe chemisorption processes (Hayward and Trapnell, 1964).

$$R_{ad,i} = k'_{a,i} \exp(-b\,\theta)\, P_i \tag{10}$$

$$R_{des,i} = k'_{d,i} \exp(b'\,\theta) \tag{11}$$

For the studied reaction, Walker and Renken (1984) observed a very strong influence of preadsorbed acetic acid on the sorption rate of ethylene, whereas the adsorption rate of acetic acid seems not to change in the range of temperature and concentration parameters studied. From their direct microgravimetric studies, they proposed a sorption model for ethylene similar to the Elovich equation. In addition, they found that the adsorption and desorption rates can be described by the same function. Based on these results, the following model is obtained, where the surface coverage θ is replaced by the concentration of adsorbed acetic acid:

$$R_{a,E} = k_{a,E} \exp(-b\,C_{A^*}) P_E - k_{d,E} \exp(-b\,C_{A^*})\, C_{E^*} \tag{12}$$

$$R_{a,A} = k_{a,A}\,(C_{\max} - C_{A^*}) P_A - k_{d,A}\, C_{A^*} \tag{13}$$

$$R_{s,EA} = k_s\, C_{E^*}\, C_{A^*} \tag{14}$$

All six parameters of the kinetic model are determined separately on the basis of individual experiments. The different experimental methods are summarized in Table 4. The numerical values of the model parameters are given in Table 5.

Table 4. Parameter Estimation

Sorption Kinetics of Ethylene	
Adsorption rate ($k_{a,E}$)	Steady state kinetics (high acetic acid concentration)
Desorption rate ($k_{d,E}$)	From adsorption isotherms (microbalance)
Inhibition constant (b)	Dynamic microgravimetric measurements
Sorption Kinetics of Acetic Acid	
Adsorption rate ($k_{a,E}$)	From adsorption isotherms
Desorption rate ($k_{d,E}$)	Transient behavior
Chemical Reaction	
Reaction rate (k_s)	Transient behavior under reaction conditions

Table 5. Model Parameters: Multistep Control, Real Surface

Symbols	Value	Unity
$k_{a,E}$	$3.0 \cdot 10^{-6}$	$\frac{\text{mol}}{\text{mol } H_2SO_4 \cdot \text{mbar} \cdot \text{s}}$
$k_{d,E}$	$1.4 \cdot 10^{-3}$	$\frac{1}{\text{s}}$
$k_{a,A}$	$1.2 \cdot 10^{-3}$	$\frac{1}{\text{mbar} \cdot \text{s}}$
$k_{d,A}$	$3.0 \cdot 10^{-3}$	$\frac{1}{\text{s}}$
k_s	$3.0 \cdot 10^{-3}$	$\frac{\text{mol } H_2SO_4}{\text{mol} \cdot \text{s}}$
C_{max}	0.45	$\frac{\text{mol}}{\text{mol } H_2SO_4}$
b	10	$\frac{\text{mol } H_2SO_4}{\text{mol}}$

Reactor Simulation

Based on the proposed models, the steady state and transient behavior of the reactor can be described satisfactorily. This is shown in Figure 2 for the steady state.

The steady state behavior can be explained in the following manner: At low acetic acid pressures, the overall reaction rate is determined by the chemical reaction and the adsorption of the acid. The rates of these steps increase gradually with increasing partial pressure of acetic acid. In contrast, the initially high rate of ethylene sorption declines with increasing acid concentration. The maximum is found in the pressure range where the rates of the different steps are comparable.

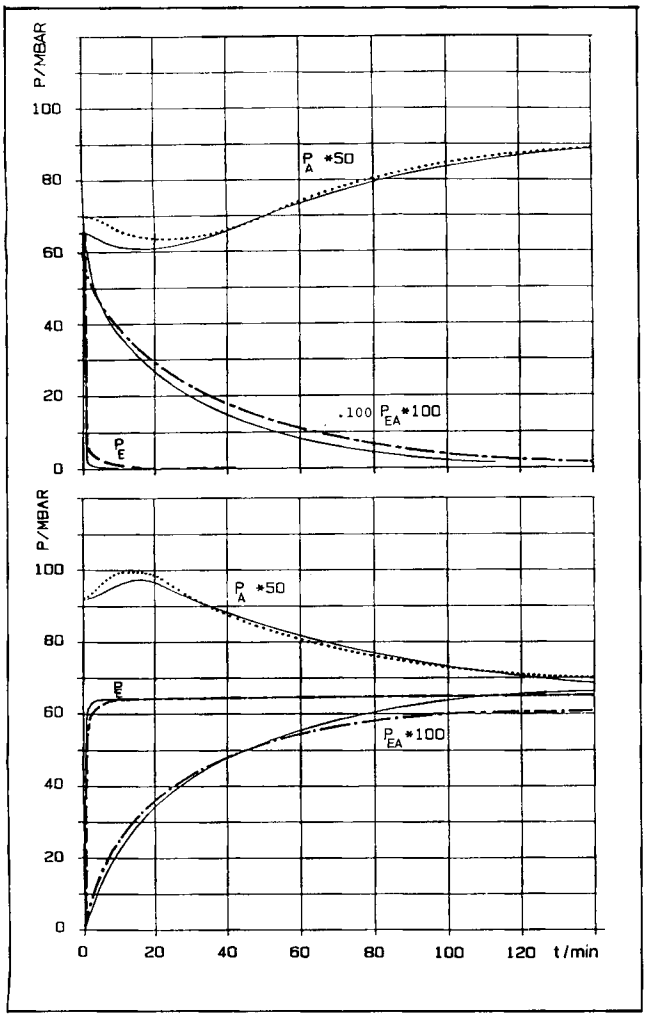

Figure 8. Measured and predicted transient behavior on stepwise variation of ethylene feed.

In Figure 8, the experimentally observed transient behavior of the reactor for a step decrease and a step increase of ethylene is compared to calculated concentration-time curves. Whereas the concentration of ethylene changes very rapidly within a few minutes, concentrations of the reaction partner acetic acid and of the product ethyl acetate reach constant values only after several hours. Due to the strong inhibition of ethylene adsorption and desorption in the presence of acetic acid, the adsorbed ethylene reacts nearly completely to the ethyl acetate before desorption occurs.

The transient behavior on variation in acid concentration is presented in Figure 9. This behavior is very characteristic of the reaction on account of the observed extremes in the concentration-time functions. The variation of ethyl acetate concentration is described in a correct way: for the start-up procedure, the catalyst is loaded with ethylene and the rate-determining step is first the sorption of acid and the chemical reaction. The result is a rather high production rate of ethyl acetate. When the adsorbed ethylene is consumed, the overall rate slows down and is finally controlled by the ethylene adsorption, a process strongly inhibited by the acid. When the acid feed is stopped, the acetic acid concentration on the catalyst drops quickly due to the chemical reaction and absence of adsorption. In consequence, the rate of reaction decreases. On the other hand, the inhibition of ethylene adsorption becomes reduced by the decrease of acetic acid concentration on the surface, and the ethylene concentration on the catalyst increases and overcompensates the first mentioned process. The overall reaction rate increases and passes a maximal value.

As pointed out earlier, a limited maximal overall reaction rate exists under steady state conditions for the type of kinetics discussed. It is interesting to note that this maximal reaction rate can be considerably increased by periodically changing the fluid phase concentration on the inhibiting reactant: in the present example, the acetic acid. However, this maximal reaction rate

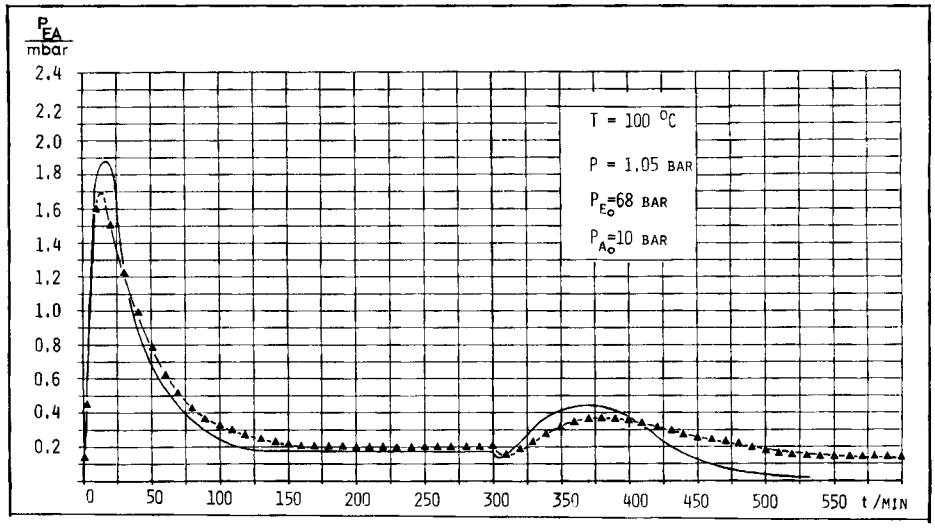

Figure 9. Measured and predicted behavior on stepwise variation of acid feed.

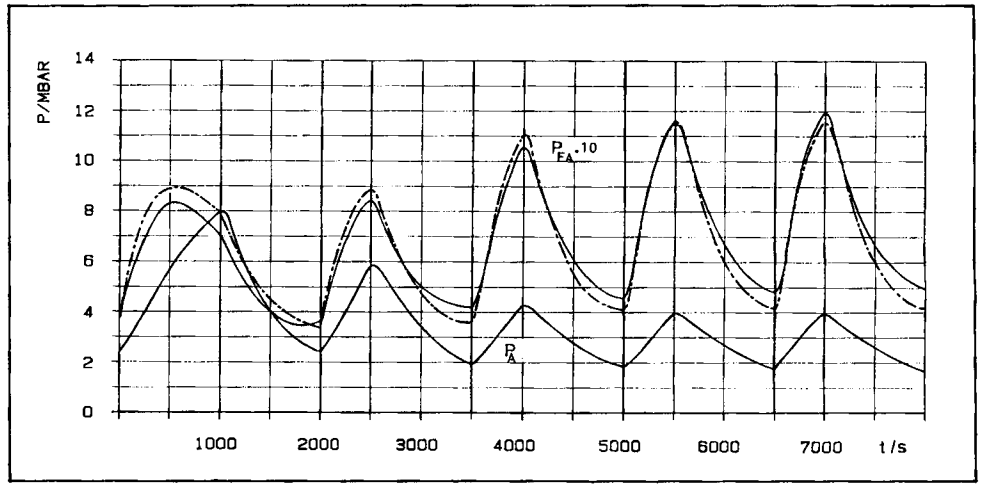

Figure 10. Measured and predicted behavior on periodic variation of acetic acid feed (start-up).
T = 110°C; P = 1.05 bar; P_{Eo} = 68 mbar

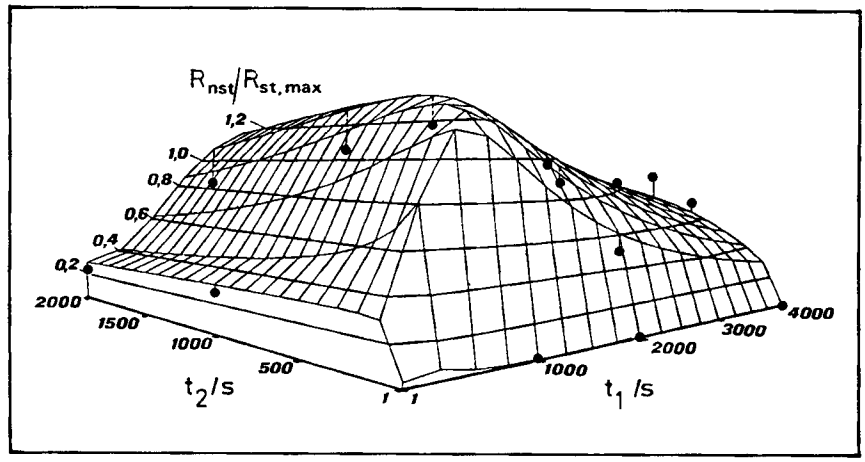

Figure 11. Predicted and measured performance at periodic operation.
P_{Ao} = 10 mbar; P_{Eo} = 68 mbar

can be increased by imposing periodic concentration fluctuations of the reaction inhibitor. Figure 10 shows the response of the differential reactor to concentration variation of the acetic acid feed in a square-wave function. The time-averaged production rate depends on the length of period and the ratio of the partial periods. For the experimental example and the chosen experimental conditions, the mean reaction rate under periodic operation is about 20% higher than the maximum steady state value, Figure 11.

The achievable rate under dynamic conditions is strongly influenced by the sorption rate of the inhibitor. Increasing sorption rates will increase the effect of periodic operation. At the same time, the optimal frequency under periodic operation is very high. For instantaneous sorption rates, highest reactor performances are found under relaxed steady state conditions. This is demonstrated in Figure 12. The simulated curves are based on experimental values, except the sorption rate of acetic acid, which is assumed to be infinite.

Discussion

Lumped reaction models based on experimental data obtained under steady state conditions are often inadequate for describing the dynamic behavior of heterogeneous catalytic reactors. For prediction of the transient behavior and the optimization of the reactor performance under periodic operation, the mechanism and dynamics of the individual reaction steps must be known in more detail. On the other hand, transient response methods in heterogeneous catalysis can be used to get more information on surface reaction and sorption kinetics and can help in model discrimination.

Acknowledgment

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Notation

a = specific surface
b = inhibition constant
C = concentration
D^e = effective diffusion coefficient
E = activation energy
k = rate constant
k_g = mass transfer coefficient
K = equilibrium constant of sorption
P = pressure or partial pressure
r_p = particle radius
R = reaction rate
R_a = sorption rate
t = time
t_1, t_2 = length of partial period
T = temperature
β = constant, Eqs. 6, 7
θ = surface coverage

Subscripts

a, as = adsorption
A = acetic acid
A^* = adsorbed acetic acid
d, des = desorption
E = ethylene
E^* = adsorbed ethylene
EA = ethyl acetate
i = reactant
nst = non-steady state
o = inlet conditions

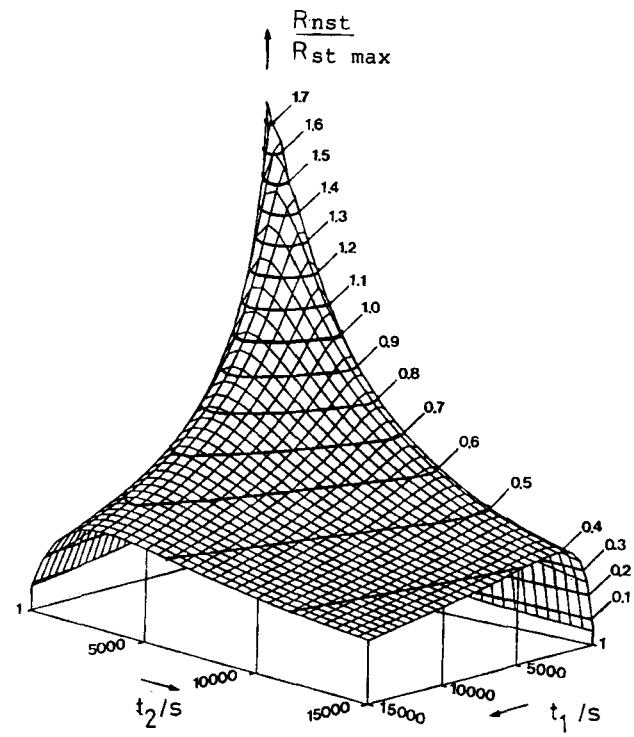

Figure 12. Predicted reaction rate at periodic operation compared to the maximal steady state value.
Instantaneous sorption rate of acetic acid.
P_{Ao} = 19 mbar; P_{Eo} = 68 mbar

ob = observed
s = surface reaction
st = steady state

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