RARE BEHAVIOUR OF A CATALYST PELLET CATALYST DYNAMICS

K.R. Westerterp, R.A. Loonen and A. Martens.

Twente University of Technology, Dept. of Chemical Technology,
Enschede, The Netherlands.

ABSTRACT

Temperature overshoots and undershoots were found for a Pd on alumina catalyst pellet in its course towards a new steady state after a change in concentration of one of the reactants ethylene or hydrogen. When cooling the pellet, after heat-up by reaction, with pure hydrogen a sudden temperature peak appears after a short time. A mathematical model is introduced, which can explain the over- and undershoots by slow adsorption on the active sites of the catalyst of one of the reactants.

KEYWORDS

Overheating of catalyst pellet, catalyst pellet temperature overshoot, catalyst dynamics, ethylene hydrogenation, palladium catalyst, slow adsorption on active sites, cooling of catalyst pellet, temperature undershoot.

INTRODUCTION

In our laboratories we investigate the behaviour of the adiabatic bed reactor, in which the acetylene in the ethylene stream from an ethylene cracker is hydrogenated. The catalyst consists of cylindrical alumina pellets with 0.08 wt % Pd. The reactor for this process in industry is known to be rather unstable tending to runaways, if not controlled very carefully. During our investigations we found for the reaction between hydrogen and ethylene that the catalyst - in the course of going after a concentration change from one steady state to a new one - does not approach the new steady state exponentially, as we would expect, but exhibits a temperature overshoot. We have reported previously [1,2] on this unfamiliar phenomenon and also have proposed a possible explanation and a model to describe these overshoots. We assumed for this reaction an Eley-Rideal mechanism, in which chemisorbed hydrogen reacts with ethylene in the gas phase; we further postulated that the ethylene slowly adsorbs on the active sites of the catalyst. Slowly the active sites are partly blocked by the inert ethylene and consequently also the reaction rate is slowly reduced until the adsorption equilibrium is reached. In the initial period, when only a low amount of C_2H_4 has been adsorbed, the reaction rate is high and the temperature of the catalyst pellet, which is being heated up by the reaction, passes through a maximum. Beyond the maximum the reaction continues to be slowed down by the adsorption.

In Fig. 1 we give a sketch of the experimental apparatus used; in Fig. 2 some experimentally observed temperature-time curves are shown for the catalyst pellet if alternately a reaction mixture or inert gas is passed through the apparatus. We see that for the reaction between ethylene and hydrogen the overshoots are reproducible.

In order to test a model for this temperature overshoot by experiments, we must have a reliable correlation for the heat and mass transfer coefficients between the catalyst pellet and the gas flowing around it. Much work has been done [3] on heat transfer to cylinders (like tube bundles in heat exchangers) but we could not find a reliable heat transfer correlation for a single cylindrical pellet and the gas flowing around it in the axial direction. We decided to determine the heat transfer coefficients directly by first heating up the cylindrical pellet by reaction and then cooling it with several inert gases. From the cooling curve the heat transfer coefficient can be derived. During these experiments we found new, rare phenomena. In this paper we now will discuss in detail the model used to interpret the overshoots, and describe the phenomena, we have not yet reported [1,2] on.

Fig. 1. The experimental set-up.

Fig. 2. A reproducibility test for the overshoot. Cooling by nitrogen; heating by reaction of 30 vol% C_2H_4 , 20 vol% H_2 and 50 vol% N_2 ; gas flow rate 0.21 m/s.

MATHEMATICAL DESCRIPTION OF THE DYNAMICS OF A CYLINDRICAL CATALYST PELLET

To describe the kinetics of the reaction between hydrogen and ethylene, we have previously postulated [1,2] an Eley-Rideal mechanism, in which chemisorbed H_2 reacts with ethylene in the gas phase [4,5]. Due to a slow adsorption of ethylene the number of active sites available for hydrogen is gradually reduced and consequently the reaction rate is slowed down. In this case the rate expression would be:

$$R'' = k'' C_{E1} \Theta_{H_2}$$

in which C_{E1} is the ethylene concentration in the gas phase at the catalyst surface and Θ_{H_2} the fraction of the active sites covered with hydrogen. In our case:

$$\Theta_{H_2} = \frac{K_H C_{H1}}{1 + K_H C_{H1} + K_E C_{Es}}$$

where C_{Es} is the concentration of the adsorbed ethylene blocking the active sites and C_{H1} the concentration of hydrogen at the interface in the gas phase. At equilibrium $m C_{E1} = C_{Es}$, in which m is the distribution coefficient. Now in case $K_H C_{H1} + K_E C_{Es} \gg 1$, we can write:

$$\Theta_{H_2} = \frac{1}{1 + K C_{Es}}$$

in which $K = K_E / K_H C_{H1}$. The mass transfer coefficient of hydrogen is higher than that of ethylene, so that $\bar{C}_H = C_{H1}$ is assumed to hold, which implicates that the hydrogen concentration approximately remains constant. For the mass transport of ethylene to the catalyst surface we have:

$$k_{GE}(\bar{C}_E - C_{E1}) = R'' = \frac{k'' C_{E1}}{1 + K C_{Es}} \quad (1)$$

For the slow adsorption of ethylene blocking the active sites a mass balance gives:

$$\frac{d}{dt} \left(\frac{C_{Es}}{m} \right) = k(C_{E1} - \frac{C_{Es}}{m}) \quad (2)$$

in which k is the adsorption rate constant. The heat balance of the particle leads to the expression:

$$\left(\frac{\rho C_p d}{6} \right) \frac{dT_1}{dt} = (-\Delta H_r) R'' - \alpha(T_1 - \bar{T}) - \sigma(T_1^4 - \bar{T}^4) \quad (3)$$

in which T_1 is the temperature of the particle and $\bar{T}$ of the bulk of the gas flowing around the pellet. In our case the length of the cylindrical pellet equals its diameter.

The equations (1) to (3) can be made dimensionless, so that we obtain:

$$\frac{dC_s^*}{d\theta} = B(C_1^* - C_s^*) - B\left(\frac{A}{1+A} - C_s^*\right) \quad (4)$$

$$\frac{dT_1}{d\theta} = \frac{P}{1+A} - (T_1 - \bar{T}) - Q(T_1^4 - \bar{T}^4) \quad (5)$$

with

$$A = A(1) + A(2) \cdot C_s^* \quad (6)$$

$$A(1) = \frac{k_{GE}}{K^n} = A^*(1) \exp(E_1/T_1) = \frac{k_{GE}}{A_K} \cdot \exp\left(\frac{E_K/RT_R}{T_1}\right)$$

$$A(2) = \frac{k_{GE} K m \bar{C}_E}{k^n} = A^*(2) \exp(E_2/T_1) = \frac{k_{GE} A_K \bar{C}_{Em}}{A_K} \cdot \exp\left(\frac{(E_K - E_K')/RT_R}{T_1}\right)$$

and with the initial conditions:

$$\begin{aligned} T_1 &= T_{10} \\ C_s^* &= C_{s0}^* \end{aligned} \quad (7)$$

Here $C_s^* = C_{Es}/m\bar{C}_E$, $T_1 = T_1/T_R$ and $\theta = t/\tau$. T_R is a reference temperature and τ the time constant for the cooling of the catalyst pellet: $\tau = \rho c_p d_p / 6\alpha$. Further $\bar{T} = \bar{T}/T_R$. In these equations a number of dimensionless groups appears, which determine the dynamic behaviour of the catalyst pellet. These groups are:

$B = \frac{\rho c_p d_p k}{6\alpha}$, the ratio of the time constant of the rate of adsorption of ethylene on the active sites to that of the rate of cooling of the pellet.

$P = \frac{(-\Delta H_r) k_{GE} \bar{C}_E}{\alpha T_R}$, is the dimensionless maximum temperature difference over the boundary layer around the pellet.

$Q = \frac{\sigma T_R^3}{\alpha}$, a measure for the potential contribution of the radiation to the heat loss from the particle.

A , the ratio of mass transfer coefficient to the kinetic constant. As follows from Eq.(1) A is also equal to the ratio of the gas concentration of ethylene at the catalyst surface to the concentration difference over the boundary layer and therefore varies from almost infinite at very low reaction rates to almost zero at complete mass transfer control of the reaction. This ratio is extremely temperature sensitive. Measures for this sensitivity are E_K/RT_R for the kinetic rate constant and E_K/RT_R for the adsorption constant K_E/K_{HCH_4} multiplied by the distribution coefficient m . The temperature independent parts of A are given by $A^*(1)$ and $A^*(2)$, moreover A depends on the concentration of ethylene on the catalyst surface C_s^* . We should realise that $(\bar{C}_E - C_{E1})/\bar{C}_E = (1+A)^{-1}$ and $C_{E1}/\bar{C}_E = A/(1+A)$.

In this model description k has been taken constant. In the experimental part we will demonstrate that most probably k is rather temperature sensitive. With this model heating and cooling curves after a concentration change can be calculated. The temperature overshoot (defined as the difference between the maximum temperature and the final steady state temperature) is very sensitive to the value of B and of A . The final steady state temperature is very sensitive to A and in particu-

Fig. 3. A temperature overshoot and undershoot as calculated with the model.

Changes of pure nitrogen to 50/50 vol% C_2H_4/H_2 and after 200 s to 30/30/40 vol% $C_2H_4/H_2/N_2$.

Data used: $k_G = 0.107$ m/s, $(-\Delta H_r) = 137$ MJ/kmol, $k^n = 3500 \exp(-4600/T_1)$ m/s, $d_p = 6.7 \cdot 10^{-3}$ m, $K = 83 \cdot 10^6 \exp(-5000/T_1)$ m³/kmol, $\rho_p = 1100$ kg/m³, $c_p = 870$ J/kg K, $k = 0.04$ s⁻¹, $\alpha = 100$ W/m²K, $\bar{T} = 300$ K, $T_{10} = 300$ K and $C_s = 0$.

Fig. 4. An experimentally produced undershoot. After a change from 50/50 vol% C_2H_4/H_2 to 5/5/90 vol% $C_2H_4/H_2/N_2$.

laid to E_1 and E_2 . Previously we have compared calculated and measured heating curves. In Fig. 3 we show a calculated heating up curve and a cooling curve. We see that the model also describes the undershoot.

In view of the high sensitivity a.o. towards the value of B , in which the pellet gas heat transfer coefficient α is included, accurate values of α must be available as a function of the system properties and the gas flow. We decided to measure α_p ourselves from cooling curves and correlate it in a $Nu = f(Re, Pr)$ relation. Some new rare phenomena were observed.

EXPERIMENTS

The experiments were carried out in the apparatus shown in Fig. 1. The overshoots found are demonstrated in Fig. 2. If temperature overshoots are found on a catalyst pellet, also undershoots must be feasible.

This is shown in Fig. 4. We see that after a sudden lowering of the reactant concentration the pellet temperature in going to the new steady state passes through a minimum. Initially too much ethylene is adsorbed which is slowly removed and thereby increasing the reaction rates.

If the active sites are partly blocked by slowly adsorbing ethylene, then a pretreatment of the catalyst pellet by ethylene should also reduce the temperature overshoot: in that case there is an excess ethylene adsorbed so that initially the reaction is inhibited. In Fig. 5 the results are shown if the pellet is pretreated with ethylene at room temperature for a certain period. After a pretreatment of two hours the temperature overshoot has completely disappeared. We have to realize that these pretreatment times are relatively long because probably at room temperature the chemisorption of ethylene is very slow. This would indicate that k is a function of temperature.

Fig. 5. The magnitude of the temperature overshoot after first the pellet has been rinsed with pure ethylene during the period t_{rinse} and then a mixture of 50/50 vol% C_2H_4/H_2 is supplied.

Fig. 6. Temperature increase of the catalyst pellet if the gas flow is switched from pure nitrogen to pure ethylene. The gas velocity is $22.7 \cdot 10^{-3} m/s$.

The adsorption of ethylene has its own heat effect. In Fig. 6 the pellet temperature is shown if at a very low flow rate nitrogen is replaced by pure ethylene. Due to the low flow rate the heat transfer coefficient and the cooling are also low. We observe two temperature maxima. The first one corresponds to the adsorption of ethylene on the palladium, which in our shell catalyst is deposited only on the outer surface of the pellet (penetration depth has been determined to be lower than 100 microns). The second maximum corresponds to the heating up of the particle by the physical adsorption of the ethylene in the pores of the pellet.

In Fig. 7 for two initial temperatures it is shown what happens if a hot particle is cooled with pure hydrogen. The particle had been heated by reaction. First the particle cools but then suddenly the particle heats up again, the temperature reaches a peak and then the particle cools again. The temperature peak is relatively high, if the starting temperature of the pellet is relatively low.

Fig. 7. Cooling curves of particles heated by reaction: cooling with pure hydrogen from a high (a) and a low (b) initial temperature.

This phenomenon can be explained as follows. As soon as the reaction mixture is replaced by pure hydrogen the pellet starts to cool; simultaneously the ethylene, which was present in the pores, is driven out of the pellet and passes the palladium on the outer surface of the pellets, where it reacts with the hydrogen. After a certain period when the ethylene adsorbed on active sites is sufficiently removed, the reaction becomes more violent and the particle is heated up again due to this reaction. When all ethylene in the pores has disappeared cooling starts again. If the initial pellet temperature is relatively low, more ethylene will be adsorbed in the pores, resulting in a relatively high peak temperature.

DISCUSSION AND CONCLUSIONS

Previously [1,2] we discussed that the magnitude of the temperature overshoot depends either on the Nusselt or on the Sherwood number. The simulation model above demonstrates that it is the Nusselt number, which strongly governs the phenomena described.

To check the validity of the model we are at present determining experimentally the steady state kinetics of the hydrogenation of C_2H_2 and of C_2H_4 , the heat transfer coefficients and the radiation heat losses. These data must be known accurately before the model can be tested experimentally and eventually improved.

In an adiabatic bed reactor we are testing the behaviour of a bed of cylindrical pellets. Also here overshoots after concentration changes are observed for the system hydrogen-ethylene. We feel that these overshoots in practice are largely responsible for the runaways of this reactor type. Moreover the phenomena observed are serious enough to put more emphasis on the study of catalyst dynamics in research and development of catalysts.

SYMBOL LIST

C	concentration	kmol/m^3
$\bar{C}$	concentration in bulk of gas	kmol/m^3
C_p	specific heat	J/kg K
d_p	particle diameter	m
E	activation energy	J/kmol
ΔH_r	reaction heat	J/kmol
k''_r	kinetic constant	m/s
k_G	mass transfer coefficient	m/s
K	chemisorption constant	m^2/kmol
m	distribution coefficient	m^2/m^3
R''	reaction rate	$\text{kmol/m}^2\text{s}$
t	time	s
T	temperature of bulk of gas	K
T_i	temperature of catalyst	K
T_R	reference temperature	K
$A, A(1), A(2), B, P, Q$	dimensionless groups, see text	-
α	heat transfer coefficient	$\text{W/m}^2\text{K}$
θ	fraction of active sites	-
σ	Boltzmann constant	-
ρ	particle density	kg/m^3

Indices

E	ethylene
H ₂ , H	hydrogen
i	at the interface gas-catalyst
s	adsorbed

REFERENCES

- [1] K.R. Westerterp, W.C. Kusters and R.J. Wijngaarden: Chem. Ing. Techn. **56** (1984), 621-624
- [2] K.R. Westerterp, W.C. Kusters and R.J. Wijngaarden: Chem. Eng. Sci. **40** (1985), 1463-1467
- [3] V. Gnielinski: Forsch. Ing.-Wes. **41** (1975) Nr 5, 145-153
- [4] I. Ratajczykowa and I. Gzymska: Chem. Physics Letters, **96** (2) (1983), 243-246
- [5] G.M. Schwab, W. Schmatz and H. Noller: Z. Phys. Chemie, Neue Folge **29** (1961), 356-370