A TEMPERATURE OVERSHOOT ON A CATALYST PELLET

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Abstract—An unexpected temperature overshoot was 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. The reaction mixture consisted of ethylene, hydrogen and nitrogen as inert. A speculative model is introduced, which can explain these overshoots by a slow adsorption of one of the reactants on the active sites of the catalyst.

INTRODUCTION

In the product separation units of ethylene cracking plants the ethylene stream contains acetylene. This acetylene has to be removed, because it hampers the ethylene polymerization. Usually this is done in a catalytic adiabatic fixed bed reactor, where the acetylene is selectively hydrogenated with an excess of hydrogen. Ideally it is converted into ethylene only, but small amounts of ethylene are also cohydrogenated. The two reactions are:

The hydrogenation reactors are known to exhibit thermal runaway rather frequently; suddenly the ethylene cohydrogenation starts full scale, thereby completely consuming the excess of hydrogen and increasing the temperature difference over the bed manifold.

A project was started in our laboratories to investigate the causes of the runaway and the dynamic behaviour of the reactor. During experiments on the reaction kinetics some unexpected phenomena were observed: it took long periods of time to reach stable conditions in a test reactor. Moreover the conversion-residence time relations showed S-shaped curves. The latter phenomenon was supposed to be caused by the catalyst switching from a lower, kinetically controlled stable operating point to the higher, mass transfer controlled stable operating point. Both observations led us to a study of the behaviour of a single catalyst pellet. In this study a temperature overshoot was observed with a time constant in the order of magnitude of minutes; it is this phenomenon that shall be reported here in more detail.

Plant conditions for the acetylene removal by hydrogenation is described in literature [1, 2, 3, 4, 5]; Lam and Lloyd [5] provide many operating details. The C_2H_2 content of the ethylene stream is usually reduced from 2000–20,000 ppm to around 1–5 ppm with a Pd catalyst on an alumina carrier. The reactor inlet temperature is 50–80°C and the exit temperature depends on the amount of hydrogen converted, the adiabatic temperature rise being 30–40°C per mole %

of H_2 converted. The reactor pressure varies from 1.0 to 3.5 MPa. Carbon monoxide is often added to the feed stream to moderate the catalytic activity and increase the selectivity. A survey of the experimental work up till 1978 on the kinetics of the reactions involved and the catalysts used is given by Webb [6]. After 1978 more experimental results were reported on by McGown *et al.*, [7, 8], Webb *et al.*, [9, 10, 11, 12] and Guzzi *et al.*, [13, 13, 15]. The literature is not conclusive as to the reaction rate equations, but all agree upon a Langmuir–Hinshelwood or an Eley–Rideal type. Most experiments were done at atmospheric pressure.

On a Pd catalyst the selectivity towards the acetylene hydrogenation is high, which is explained by the strong adsorption of C_2H_2 . Probably C_2H_2 and C_2H_4 are adsorbed on different sites and the C_2H_2 is replaced by H_2 , as it is consumed. The selectivity deteriorates, when the C_2H_2 is replaced by H_2 . CO adsorbs on the same sites as H_2 , an addition of CO leads to a reduction of the catalyst activity, but restores its selectivity. Beeck [16] reported on a reversible deactivation of the catalyst without mentioning an influence on the catalyst pellet temperature.

Catalyst pellets can exhibit multiplicity and instabilities, e.g. oscillations. These phenomena are amply discussed in the literature, e.g. in reviews by Luss [17], Schmitz [18], Sheintuch and Schmitz [19] and Bennett [20]. Luss derived criteria for uniqueness and multiplicity of a catalyst pellet [21]. Oscillations have been studied experimentally mainly for the oxidation of H_2 or CO [19]. The temperature in a catalyst pellet is not uniform for particles with low thermal conductivities, criteria for isothermicity were given by Anderson [22], experimental work is reported on a.o. by Irving and Butt [23], Furasawa and Kunii [24] and Hughes and Koh [25]. Elnashaie and Cresswell [26, 27, 28] a.o. introduced Langmuir–Hinshelwood kinetics in the study of catalyst pellet behaviour. The mathematics required for the study of catalyst behaviour are thoroughly discussed by Aris [29].

Concentration overshoot phenomena on catalyst pellets after a step disturbance in the bulk temperature or concentration have been summarized by Bennett [20]. For temperature overshoot phenomena

after a step disturbance we could not find any reference in the literature; we used the search words "dynamics", "catalyst pellet", "thermal . . .", "temperature . . ." and "overshoot". In studies on the hydrogenation of ethylene and multiplicity [24, 25] temperature overshoots were not mentioned; Ni on alumina-silica [25] and CuO/Cr₂O₃/MnO₂ [24] were used as catalysts. Dettmer and Renken [30] indicated slow chemisorption as the cause of a concentration overshoot in an isothermal experimental reactor.

EXPERIMENTS

Experiments on a single catalyst pellet were executed at atmospheric pressure in a glass tube as shown in Fig. 1. In order to avoid heat losses due to conduction along the thermocouple wire, three additional catalyst pellets were mounted on the wire free from and above the main pellet of which the temperature was measured. The three other pellets will exhibit the same temperature behaviour as the main particle, so that the temperature difference along the wire is zero and heat losses due to the wire can be neglected. The temperature of the gas before and after the pellets is measured too. The gas flows upward through the tube and can be preheated, flow rate and temperature can be changed, while flow rates are measured with rotameters. Concentrations in the gas can be varied by feeding varying quantities of C₂H₄, H₂ (and N₂). Two types of catalysts were used: cylinders and spheres. In the cylindrical pellet we installed two thermocouples, one with the joint in the centre and one on the outer surface, according to the experimental technique of Wicke [31]. As no temperature difference could be detected between the centre and the surface, the spherical pellets were equipped only with one ther-

mocouple with the joint in the centre of the pellet. The pellet heat conductivity is apparently large. The cylinder is an industrial pellet, see data in Table 1; it is a shell catalyst of the egg shell type, the maximum penetration of the Pd was less than 0.1 mm. The spherical particles were prepared by ourselves, contained 0.025 wt % of Pd on alumina and had a diameter of 6.7 mm.

Most experiments were done with spherical particles, because of the availability of correlations for the Nusselt and Sherwood numbers. Experiments were started by passing N₂ through the tube during approx. half an hour. Then we switched to a stream containing C₂H₄ and H₂ (and in many experiments N₂ as a diluent) and the temperature of the pellet was observed as a function of time. In Fig. 2 an example of the result is given: the pellet is rapidly heated up, reaches a maximum temperature $T_{\max}$ and then the temperature drops slowly till after about half an hour a steady state temperature is reached. The temperature overshoot ΔT_{OS} is completely reproducible as is shown in Fig. 3, where the same experiment was repeated eight times. The overshoot phenomenon is not only found after "start-up" of the catalyst particle, but also at changing of conditions as shown in Fig. 4, where the N₂ diluent was replaced by H₂. Overall conversions after the four pellets are so low, that the bulk of the gas is hardly heated up. Depending on the gas flow rate the conversions varied from 0.001 to 0.04 with an average of 0.004, which under adiabatic conditions would correspond to a temperature increase of the bulk of the gas after the first particle of 3–4°C.

In Fig. 5 ΔT_{OS} as observed is plotted as a function of the Sherwood number and in Fig. 6 as a function of the bulk temperature of the gas. The *Sh* number is calculated with the relation: $Sh = 2.0 + 0.66$

Fig. 1. The experimental set-up. Data: $d_p = 6.7 \times 10^{-3}$ m, tube inner diameter = 15×10^{-3} m.

Table 1. Catalyst properties

Cylinders, diameter 4.39 mm, height 4.38 mm
Catalyst density 1300 kg/m ³ , bulk density 780 kg/m ³
Active metal surface: 350 m ² /kg
Internal surface: 180,000 m ² /kg
Pd content: 0.08 wt %
Pore volume: 0.153×10^{-3} m ³ /kg
Special pellets, diameter 6.7 mm and Pd content: 0.025 wt %

Fig. 2. An experimental curve. Data: spherical particle, gas composition 50% C₂H₄ and 50% H₂, gas flow rate 0.62 m/s.

Fig. 3. A reproducibility test. Data: spherical particle, gas composition 30% C_2H_4 , 20% H_2 and 50% N_2 , gas flow rate 0.21 m/s.

Fig. 4. An overshoot after a concentration change from 17% C_2H_4 , 11% H_2 and 72% N_2 to 17% C_2H_4 and 83% H_2 at 150 s. Data: spherical particle, gas flow rate 1.27 m/s.

Fig. 5. The temperature overshoot as a function of the calculated Sherwood number.

$Re^{0.5} Sc^{0.33}$. The Reynolds number is taken at the velocity of the gas around the pellet and based on the empty cross-section. Physical properties are taken at the average film temperature. In Fig. 7 T_{max} as observed is plotted as a function of the mole fraction H_2 in H_2 - C_2H_4 mixtures. The maximum temperature is approximately linearly dependent on the H_2 mole fraction if ethylene is present in excess.

Fig. 6. The temperature overshoot as a function of the temperature of the bulk of the gas. Flow rates are 0.21 m/s (Δ) and 0.62 m/s ($\bullet$), spherical particles.

Fig. 7. The maximum particle temperature after start-up as a function of the H_2 mol fraction in the gas. Ethylene in excess. Flow rates 0.21–0.88 m/s, spherical particles.

The experimental results indicate, that the maximum pellet temperatures strongly depend on the gas composition and that the temperature overshoots do depend on the gas flow rate and gas composition, but hardly do so on the temperature of the bulk of the gas. A cross plot indicates that ΔT_{0s} is approximately $\propto \sqrt{Re}$.

A POSSIBLE INTERPRETATION OF THE EXPERIMENTS

As discussed by Westerterp *et al.* [32] for complete mass transfer resistance the pellet temperature would be:

$$T_i - \bar{T} = \frac{k_G}{\alpha} \bar{c} (-\Delta H_r) = \Delta T_{ad} Le^{-0.67}.$$

The influence of the Lewis number Le was proven by Wicke [33]. If applied to our system and to a 1:1 mixture of C_2H_4 and H_2 we would find $\Delta T_{ad} \approx 1500$ K for the adiabatic temperature rise, while the catalyst particle reached maximum temperature differences with respect to the surrounding gas of around 300°C only, see Fig. 7. This means that our experiments are *not completely mass transfer controlled*. They also can *not be pore diffusion controlled*, because we have a shell catalyst with an extremely thin layer of Pd on the outer surface. They also can *not be pellet heat conduction controlled*, because we could not detect any temperature difference between the centre and the outer surface of the pellet; with our instrumentation we should have detected a temperature difference of 0.5°C. There is also *no permanent deactivation of the catalyst* because of the full reproducibility of the experiments, see Fig. 3. So we may conclude that the overshoot phenomenon is partly mass and/or heat

transfer controlled (because of the influence of Re) and partly kinetically controlled. In the initial stage the chemical rate is high, but it is gradually slowed down due to some reversible kinetic mechanism.

As a possible explanation—which we cannot prove—we assume a slow adsorption on the catalyst of one of the components taking part in the reaction. Further we assume an Eley–Rideal mechanism, in which the chemisorbed hydrogen reacts with ethylene in the gas phase. Due to the slow adsorption of ethylene the number of active sites available for hydrogen is gradually reduced: the reaction rate is slowed down. For an Eley–Rideal mechanism with chemisorbed hydrogen reacting with gaseous ethylene and with the active sites partly blocked by adsorbed ethylene, we would have the following rate expression:

$$R'' = \frac{k'' K_H c_{H_i} c_{E_i}}{1 + K_H c_{H_i} + K_E c_{E_s}}$$

Now assuming that $K_H c_{H_i} + K_E c_{E_s} \gg 1$ and dividing by $K_H c_{H_i}$ we obtain the simplified rate expression:

$$R'' = \frac{k'' c_{E_i}}{1 + K c_{E_s}} \left(\frac{\text{moles converted}}{\text{m}^2 \text{ outer surface s}} \right) \quad (1)$$

in which $K = K_E/K_H c_{H_i}$, c_{E_i} the concentration of ethylene in the gas phase at the outer surface of the catalyst pellet (mol/m^3) and c_{E_s} of the adsorbed ethylene (mol/kg catalyst). As the mass transfer coefficient for hydrogen is around $4 \times$ higher than that for ethylene, we assumed c_{H_i} constant during an experiment. For the mass transport to the catalyst surface holds:

$$k_{GE}(\bar{c}_E - c_{E_i}) = R'' \quad (2)$$

if the accumulation of mass in the surrounding film is neglected. For the slow adsorption of ethylene, blocking the active sites, a mass balance gives:

$$\frac{dc_{E_s}}{dt} = k(m c_{E_i} - c_{E_s}). \quad (3)$$

Here m is a distribution coefficient, which has been determined with the Thermogravimetric Analyser. k is a transfer coefficient. The heat balance of the particle leads to the following expression:

$$(\rho c_p)_c \frac{dT_i}{dt} = (-\Delta H_r) R'' - \alpha(T_i - \bar{T}) - \sigma(T_i^4 - \bar{T}^4) \quad (4)$$

in which $\bar{T}$ is the temperature of the bulk of the gas and T_i of the catalyst particle. The heat losses due to radiation could not be neglected. In our case the tube wall temperature is equal to the temperature in the bulk of the gas. With eqs (1), (2), (3) and (4) an experimental curve was approximated. As fitting parameters k and K were used. The results for one experiment are given in Fig. 8, together with the mathematical approximation. For the activation energies data from literature were taken [16]. The approximation reasonably covers the measured data. We did not apply a regression analysis, because of the

Fig. 8. Measured points and calculated curve. Data used: $\alpha = 142 \text{ W/m}^2\text{K}$, $k_G = 0.107 \text{ m/s}$, $c_E = 20.2 \times 10^{-3} \text{ kmol/m}^3$, $k'' = 3500 \exp(-4600/T_i) \text{ m/s}$, $K = 65 \times 10 \exp(-5500/T_i) \text{ kg/kmol}$ and $k = 0.025 \text{ s}^{-1}$. Further $Re = 190$ and 50 vol % $\text{C}_2\text{H}_4/50 \text{ vol \% H}_2$.

speculative nature of the model interpretation of the overshoots. Also a Langmuir–Hinshelwood mechanism can be used to explain the temperature overshoot, essential is only the slow adsorption.

DISCUSSION

From Fig. 5 we can see that the temperature overshoot is approximately linearly dependent on the Sherwood number Sh for the pellet. A fit would give $\Delta T_{OS} = 2.6(Sh - 2.0)$. At no flow of gas around the particle ($Sh = 2.0$) there would be no temperature overshoot. However, we cannot distinguish whether it is the Nusselt number Nu or Sh , which is the relevant parameter, because of the Chilton–Colburn analogy. If Sh is higher, the concentration of the reactants at the interface is higher and so are the reaction rates, so the particle is heated up quicker. The simultaneous but slow adsorption in the meantime has not yet reached a stage where the reaction is seriously slowed down. Simultaneously, if Nu is higher, the heat loss rate from the particle is higher and the pseudo steady state between heat production and heat loss is reached quicker, whereas in the meantime the slow adsorption continues. Consequently temperature overshoots are larger at higher Sh -numbers or Nu -numbers. We feel that the ratio k_G/kd_p or $\alpha/\rho c_p k d_p$ is determining the magnitude of the temperature overshoot.

We realise that this interpretation to explain the temperature overshoot is speculative. For example, it is a known fact that adsorption energies on catalyst surfaces vary with the surface coverage. Therefore, it might be possible, that the temperature overshoots observed are related to the strong coverage-dependency of the catalytic activity. Moreover, it has been observed by Konvalinka and Scholten [34] in temperature programmed desorption experiments for H_2 adsorbed on a Pd catalyst on activated carbon particles, that the temperature programmed patterns shift to higher temperatures when the heating rate is increased [35, 36]. This indicates that the desorption of hydrogen is a slow process, so we cannot distinguish

between C_2H_4 or H_2 as the slowly ad- and desorbing component. Many more experiments are required to elucidate the true mechanism causing the temperature overshoots.

We are now cooperating with Professor Wicke, Institut für physikalische Chemie, Universität of Münster, FRG, to study the phenomena on the catalyst surface. In our own experimental program in the meantime we have produced a.o. temperature undershoots and also temperature overshoots at only cooling with pure hydrogen of a catalyst particle, which had been heated up previously by reaction. We further have observed the thermal behaviour of the particles for adsorption without reaction. We will report on our further experiments in due time.

We hope that at least it has become clear that we must dedicate more effort to the study of catalyst dynamics. The overshoot after a concentration change—for the industrial, cylindrical catalyst we have measured values of ΔT_{OS} of even $60^\circ C$ —are of real importance, because they are high enough to initiate the ethylene hydrogenation in an acetylene removal reactor and to cause in that way the runaways that occur in industrial practice.

NOTATION

c_p	specific heat, J/(kg K)
c	concentration, mol/m ³
$\bar{c}$	concentration in the bulk of the gas, mol/m ³
D	gas diffusion coefficient, m ² /s
d_p	pellet diameter, m
$-\Delta H_r$	reaction heat, J/mol
k	adsorption rate coefficient, s ⁻¹
k''	kinetic rate constant, m/s
k_G	mass transfer coefficient, m/s
K	adsorption constant, kg catalyst/mol
Le	Lewis number: $\lambda/\rho c_p D$
m	distribution coefficient, m ³ gas/kg catalyst
Nu	Nusselt number $\alpha d_p/\lambda$
R''	reaction rate per unit of surface area, mol/(m ² s)
Re	Reynolds number ud_p/ν
Sh	Sherwood number $k_G d_p/D$
T	temperature, K
T	temperature of the bulk of the gas, K
ΔT_{ad}	adiabatic temperature rise, K
u	linear gas velocity, m/s
α	heat transfer coefficient, W/(m ² K)
λ	gas heat conductivity, W/(mK)
ν	gas kinematic viscosity, m ² /s
σ	Stefan-Boltzmann constant, W/(m ² K ⁴)

Subscripts

c	of the catalyst
E	of ethylene
H	of hydrogen
i	at or of the pellet

max	highest temperature reached
OS	overshoot
s	adsorbed

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