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Unstable and Oscillatory Behaviour in Heterogeneous Catalysis

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Adsorption / Katalyse / Kinetische Oszillationen / Oberflächenerscheinungen / Reaktionskinetik

With two examples, the oxidation of H_2 and CO on Pt carrier catalysts, it is shown that special states of chemisorption and kinetics of surface processes can create periodicity and bistable behaviour of catalytic reactions. The (nonisothermal) oscillations of the H_2 oxidation can be traced back to the superposition of a slow oxidation-reduction process under participation of an active and an inactive (blocking) chemisorption species of oxygen, in agreement with TDS measurements. By means of a stability analysis, based on the linearized balance equations, the main features of the oscillatory behaviour can be explained. – With the CO oxidation oscillations under isothermal conditions have been studied that appear as precursors to a quenching of the reaction. A periodic change of the CO coverage (blocking) of the catalyst surface was demonstrated. For the formation of the CO coverage via CO clusters on the surface, in the sense of dissipative structures, a mechanism with co-operation of the chemisorption process and the LH-reaction is shown up. The periodic reactivation of the surface is attributed to the increase of desorption probability (decrease of desorption energy) with increasing packing density of the CO. A quantitative treatment, however, is not yet possible at present, because relationships for the kinetics of non-random distributions on surface sites are missing.

1. Introduction

The scope of the following report will not be a systematic review of the field of oscillations in heterogeneous catalysis; such reviews have been performed recently in an excellent manner by Schmitz and Sheintuch [1], and by Slinko and Slinko [2]. From these surveys it became clear that no general lines of understanding oscillatory behaviour in catalysis can be drawn as yet. The phenomena are rather manyfold, and the experimental experience is still small, incomplete, and also not fully reliable frequently, because it is not sufficiently known what are the most important variables and conditions for periodicity and unstable steady states. On the other hand, there has been extreme fertility of mathematical theories in the field, but nevertheless the progress in understanding the observable phenomena along this way is modest, and frequently restricted to formalisms. The deficiency in knowledge comes obviously from the fact that in many cases the reason for oscillatory behaviour lies in structural features of chemisorbed species, or of the catalyst surface itself. Such structural changes, however, can be detected and investigated only by experimental research, making use of the methods of chemisorption and reaction kinetics, as well as of spectroscopic means for discern and characterization of surface states. As a matter of fact, a number of authors working experimentally in the field agree to this demand and follow the same line. This line will be illustrated in the following by two examples that have been investigated thoroughly since a couple of years in our group: the oxidation of hydrogen [3], and the oxidation of carbon monoxide [4–6] on supported platinum catalysts. These are the same reactions in the course of which oscillations have been observed rather early by Beusch and by Fieguth [7, 8], as was reported first in 1970 [9, 10].

2. Hydrogen Oxidation

2.1. Experimental Methods and Results

The principle of the arrangement is shown in Fig. 1: A single catalyst pellet, 8 mm diameter, of silica-alumina with 0.4%

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platinum is exposed to the gas flow, normally air with a few percent of hydrogen. The internal surface is small – only about 450 cm^2 in macropores with $r_p \approx 3$ µm in the pellet – and the platinum impregnation covers only an outer shell of 1 mm thickness. No influence of pore diffusion, therefore, needs to be considered. The catalyst temperature is measured by a thermocouple in the center of the pellet, the chemical conversion is determined by infrared analysis for water vapor in the effluent. In a certain range of parameter values – Fig. 2: 2 to 8% of H_2, gas inlet temperature between 30 and 130 °C – oscillations of reaction rate and of catalyst temperature set in spontaneously. The frequencies increase and the amplitudes decrease towards higher temperatures. The average temperature of the catalyst pellet is about 100 K higher than the gas temperature. The wedge-shaped field of oscillations changes its position when the conditions of heat removal change (for instance by replacing the N_2 in the air by He), thereby indicating that the oscillation regime is related to the heat exchange with the surroundings. The characteristic shapes of the oscillations become clearer from Fig. 3. At lower temperatures unsymmetrical shapes develop with broad valleys and sharp peaks, indicating that a slow process with activation energy changes the state of the surface. Near the upper limit of the oscillation field the shape changes to relaxation oscillations. Remarkable are the large amplitudes of ±30 K, the long periods of 20 to 50 min, the coincidence of shape and phase in the oscillations of temperature and reaction rate, and finally the narrow range of hydrogen content in the gas phase across the field of oscillations.

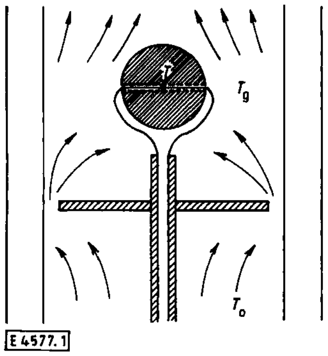

Fig. 1
Catalyst pellet with thermocouple in double-walled reactor tube [3a]. T_0 = gas inlet temperature, T_g = mean temperature of the gas flow round about the pellet (similar to a stirred tank reactor). Same type of catalyst – details see text – as used by Beusch [7]

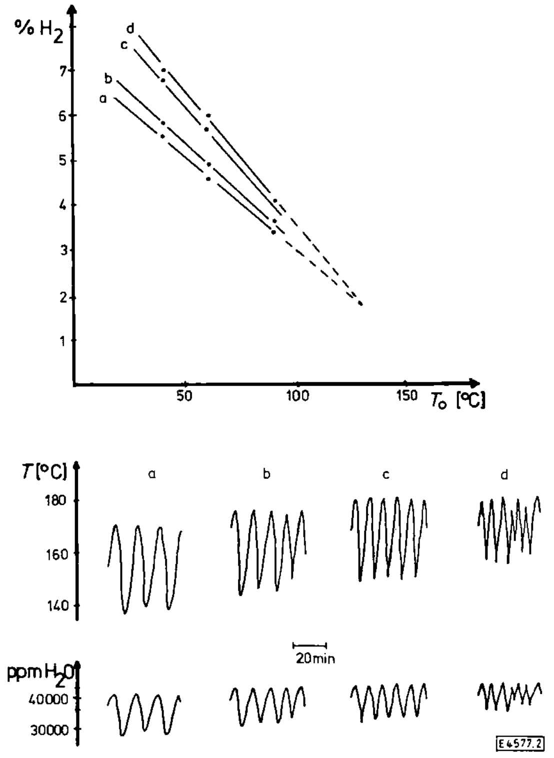

Fig. 2
Above: Region of oscillatory behaviour in the field: % H_2 in air vs. gas inlet temperature T_0 [3a] (T_0 is equal to the temperature fixed in the double wall of the reactor tube, Fig. 1).
Below: Oscillations of catalyst temperature and conversion (ppm H_2O in the effluent) across the region a → d at T_0 = 60 °C. Gas flow rate always u_0 = 0.7 cm/s under normal conditions (1 bar, 20 °C) in the empty tube

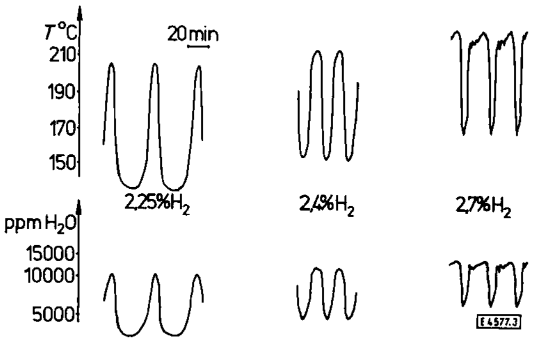

Fig. 3
Shapes of oscillations at higher gas flow rate [3a].
u_0 = 2.1 cm/s, H_2 in air, T_0 = 90 °C

In contrast to this, the range of oxygen concentrations wherein oscillations occur is very broad, and extends, as Fig. 4 shows, from less than 10 to more than 50%. But the shapes of the oscillations and their changes with increasing temperature are similar to those in Fig. 3. It can be concluded from this behaviour that the oxygen covers largely the catalyst surface and retards the reaction rate. At temperatures around 200 °C the reaction rate indeed decreases with increasing oxygen content in the gas flow as is shown in Fig. 5. At lower catalyst temperatures (95 °C) the reaction rate increases smoothly with oxygen partial pressure up to a saturation limit; in this range no oscillations can be observed. At higher temperatures, however, the reaction rate runs through a maximum; the descending branch towards higher oxygen contents represents the region where oscillations occur (with hydrogen contents higher and flow rates lower than those applied here in order to avoid oscillations). Measurements at intermediate temperatures, carried out for determining an overall activation energy, indicated the retardation effect of the oxygen becoming remarkable above about 120 °C. By adding small amounts of CO – for weakening the O_2 chemisorption – the retardation could be partly removed. From these findings it can be supposed that part of the chemisorbed oxygen changes from an active species to an inactive one which blocks up part of the catalyst surface for the reaction.

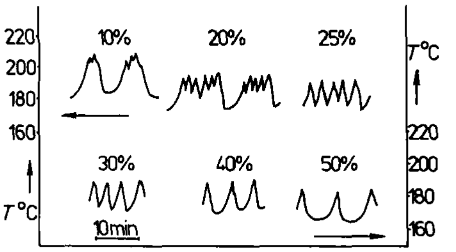

Fig. 4
Oscillations of catalyst temperature at different O_2 concentrations, increasing from 10 to 50% O_2 in N_2 with 6% H_2 [3]. u_0 = 0.7 cm/s; T_0 = 60 °C

Similar oscillations as presented in Fig. 3 have been obtained with an "artificial" catalyst pellet, made up of a short end of a Pt tube, 0.6 cm in diam., 1 cm high, the external surface of which was covered with Pt black. The activity was similar to that of the "genuine" pellet; the same heat capacity was approached by putting a small copper cylinder into the tube, in order to obtain similar oscillation periods. These observations make sure that the oscillations are not a peculiarity of a special type of supported Pt, but are an inherent property of platinum as an oxidation catalyst.

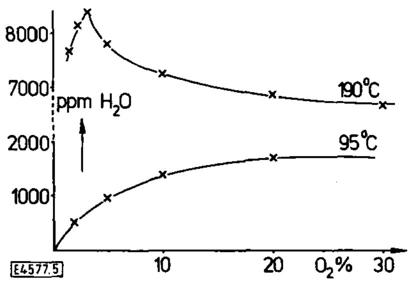

Fig. 5
Reaction rate under steady-state conditions as function of O_2 concentration at lower (95 °C) and higher catalyst temperatures (190 °C). u_0 = 3.5 cm/s, 1% H_2 in O_2/N_2 mixture

In order to search for different species of chemisorbed oxygen, use was made of the method of desorption spectroscopy (TDS) with thin Pt wires (0.1 mm) under high vacuum conditions. Fig. 6 represents part of the results: Desorption runs with different oxygen charging pressures in the range of 10^{-6} mbar reveal a peak and a shoulder, indicating two species α and β with desorption temperatures of 420 and about 720 °C. These temperatures correspond to desorption energies of 175 and 235 kJ/mol, in fair agreement with literature data from TDS investigations [11–13]. We identify the α species with the active type and relate the β species with the blocking type of chemisorbed oxygen.

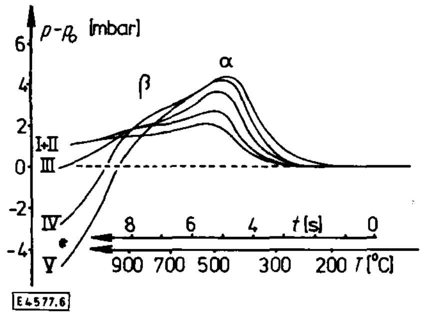

Fig. 6
Thermal desorption spectra of O_2 from a polycrystalline Pt wire (0.1 mm) at different basic O_2 pressures p_0 for chemisorption at normal temperatures. Curves I to V correspond to $p_0 = 3.5 \cdot 10^{-7}$ mbar, 4.8, 9.0, 22, and $27 \cdot 10^{-7}$ mbar, respectively [3]. (The run of the curves IV and V into negative $(p - p_0)$ values at high wire temperatures is to be attributed to the consumption of oxygen for burning off small amounts of CO, H_2 and hydrocarbon impurities.)

The existence of two types of surface oxygen like these has been stated in recent years in several investigations that have been performed under UHV conditions applying AES, LEED, and flash desorption techniques on Pt(110) planes [14, 15] as well as AES on polycrystalline Pt [16]. There is agreement in the observations that oxygen chemisorbed below about 800 K reacts readily with H_2 or CO, but that chemisorption at about 1000 K or above leads to tightly bound oxygen that can not be removed from the Pt surface by H_2 or CO under UHV conditions. This oxygen is considered as initiating an epitaxial growth of Pt oxide [14], and therefore may be made responsible for the platinum losses of the wire gauzes in ammonia oxidation by volatile Pt oxides.

Regarding this tightly bound oxygen, two remarks may be made. First: Surface oxygen species that are formed by chemisorption of O_2 from the gas phase above 800 K may well be formed during reaction with H_2 at lower temperatures; this holds, particularly, for precursor states of the high temperature surface oxide. Second: The statement that an oxygen surface species is inert to exposure to H_2 (or CO) under UHV conditions does not exclude slow reaction under normal conditions during the rather long time intervals of the oscillation periods: 5 to 50 min (see Figs. 2 and 3).

2.2. Discussion and Mechanism of the Oscillations

Considering the sum of the foregoing arguments, the occurrence of the oscillations of reaction rate may be traced back to the competition of two processes: the blocking of active sites of the catalyst surface by an inactive oxygen species that can be taken as a precursor of a surface oxide, and the subsequent regeneration of the catalytic activity by the removal of this oxygen in a slow reduction process. The mechanism along which the two competitive processes cooperate may be set up in the following way.

The hydrogen oxidation as the main reaction that generates the heat at the catalyst pellet runs rather fast through a number of steps, for instance (1) to (4):

$$H_2 + O^*_{ad} \longrightarrow OH_{ad} + H_{ad} \tag{1}$$

$$O_2 + H_{ad} \longrightarrow OH_{ad} + O^*_{ad} \tag{2}$$

$$H_2 + OH_{ad} \longrightarrow H_{ad} + H_2O_g \tag{3}$$

$$OH_{ad} + H_{ad} \longrightarrow H_2O_g \tag{4}$$

where O^*_{ad} represents the active species of chemisorbed oxygen. The details of these steps are not of primary interest here. The overall reaction rate can be described by:

$$\dot{n}_{H_2O} \equiv r = k_r(T) \cdot (1 - \theta_0) \cdot f(p_{H_2}, p_{O_2}) \tag{5}$$

where the function f of partial pressure dependences contains – at temperatures above 120 °C – a first order relation for the hydrogen and a negative order (see Fig. 5) for the oxygen. For the following it is important that the overall reaction rate increases with temperature – in the present case with an activation energy of k_r of about 33 kJ/mol [3] – and that it is retarded by the blocking oxygen that covers the part θ_0 of the active surface sites. The change with time of θ_0, increasing by the blocking effect, and decreasing by the reactivation with hydrogen:

$$O^*_{ad} \xrightarrow{k_{bl}} O_{bl}\,; \quad H_2 + O_{bl} \xrightarrow{k_{re}} OH_{ad} + H_{ad} \tag{6a, b}$$

can be described by the blocking balance:

$$\dot{\theta}_0 = r_{bl} - r_{re} = k_{bl}(T) \cdot (1 - \theta_0) - k_{re}(T) \cdot \theta_0 \cdot \varphi(p_{H_2}) \tag{7}$$

and runs rather slow (as the difference of two nearly compensating terms). The rate of the main reaction, Eq. (5), therefore follows the changes of surface blocking, θ_0, in a quasi stationary way. The same holds for the chemical heat generation that counteracts the heat losses of the catalyst pellet to the bypassing gas flow, as it is represented by the heat balance:

$$m_p c_p \cdot \dot{T} = -\Delta H \cdot r - h \cdot A \cdot (T - T_g)\,. \tag{8a}$$

m_p and c_p mean the mass and the specific heat of the catalyst pellet, ΔH the reaction enthalpy, h the heat transfer coefficient at the surface of the pellet (surface area A), and $T - T_g$ the difference between the temperatures of the pellet (T) and of the bypassing gas (T_g). It is suitable to divide Eq. (8a) by $m_p c_p$; with the notations: $-\Delta H/m_p c_p \equiv \Delta T_a$ (type of an adiabatic temperature difference), and $hA/m_p c_p \equiv \kappa$ (cooling coefficient) the balance then reads:

$$\dot{T} = \Delta T_a \cdot r - \kappa \cdot (T - T_g)\,. \tag{8b}$$

The blocking balance (7) and the heat balance (8b) are the two differential equations which determine the dynamical behaviour of the system. Vanishing values of the time derivatives define the steady states. Within the range of parameter values where oscillations occur a stable steady state was never observed. One has to conclude therefore that in this range only one steady state exists which is dynamically unstable.

A stability analysis for the region nearby the steady state can be made readily by means of the linearized balance equations:

$$\dot{\theta} = a_{11}\,\Delta\theta_0 + a_{12}\,\Delta T \tag{9a}$$

$$\dot{T} = a_{12}\,\Delta\theta_0 + a_{22}\,\Delta T \tag{9b}$$

where the $\Delta\theta_0$ and ΔT represent the distances from the steady-state values θ_{0s} and T_s. The solutions of (9a, b) are exponential functions of time with the relaxation constants (roots):

$$\lambda_{1,2} = \frac{a_{11} + a_{22}}{2} \pm \frac{1}{2}\sqrt{(a_{11} - a_{22})^2 + 4 a_{12} a_{21}}\,. \tag{10}$$

The coefficients a_{ik}, obtained by partial differentiation of the right hand terms of the balances (7) and (8b) for θ_0 and for T, take the form:

$$a_{11} = -k_{bl} - k_{re}\,\varphi(p_{H_2})(<0)\,; \quad a_{12} = (r_{bl} E_{bl} - r_{re} E_{re}) \frac{1}{R T_s^2}$$

$$a_{21} = -\Delta T_a \frac{r_s}{1 - \theta_{0s}}\ (<0)\,; \quad a_{22} = \Delta T_a r_s \frac{E}{R T_s^2} - \kappa\,.$$

A necessary condition for obtaining self-sustained oscillations – that generally extend beyond the linear region round about the steady state – is that the $\lambda_{1,2}$ have complex values and $a_{11} + a_{22}$ be positive. As the coefficient a_{21} is always negative – due to the retardation by the blocking effect – the coefficient a_{12} must have positive values in order to obtain complex roots. Since in the range of oscillations the rates of blocking and of reactivation cancel in average: $r_{bl} = r_{re}$, this means, that the activation energy of the blocking process, E_{bl}, must be higher than that of the reactivation, E_{re}. The Arrhenius lines, accordingly, have different slopes (see Fig. 7), indicating that in the temperature peaks of the oscillations the blocking process prevails and leeds to decrease of the main reaction rate and thereby of the temperature, whereas in the temperature valleys the reactivation prevails and accelerates the reaction rate. When the mean catalyst temperatures are rather low and the amplitudes large (Fig. 3, left-hand), the small value of r_{re} at T_{min} (Fig. 7), and the large value of r_{bl} at T_{max} determine the shape of the oscillations: broad minima, indicating the slow regeneration process, and narrow peaks, characteristic of quick blocking. At higher mean temperatures – and accordingly higher hydrogen contents (Fig. 3), right-hand – the regeneration process is favoured; the main reaction rate tends to stay in the maximum region, and breaks down for short periods only. At slightly higher hydrogen contents these breaks become smaller and finally vanish within the random scatter of temperature and concentration measurements.

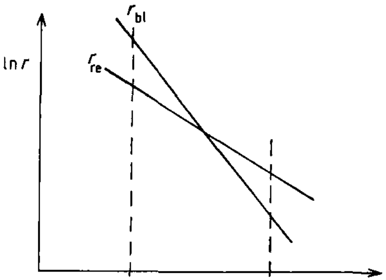

Fig. 7
Rate of blocking (r_{bl}) and of reactivation (r_{re}) in the Arrhenius-diagram; schematic

The second condition for steady oscillations: $a_{11} + a_{22} > 0$, demands that a_{22} should take positive values (because a_{11} is a small negative quantity). Since a_{22} is a difference of two terms – temperature derivatives of the heat generation and of the heat removal – these terms cancel approximately within the parameter range where the oscillations occur. Their difference therefore is small compared with the absolute values, this means that only a small excess of the total heat production brings about the periodical heating up of the pellet, and a small deficiency the cooling. Accordingly small – a few percent only – are the fractions of the active sites in the catalyst surface which must be affected by the blocking and the reactivating process in order to create oscillations.

Regarding the compensation of the chemical heat production and the convective heat removal in the region of oscillations, the influence of the gas flow rate is interesting. Fig. 8 represents this influence in the % H_2 vs. u_0 plane at fixed gas inlet temperature. With growing gas flow rate the heat production increases – because the level of the H_2 concentration at the pellet surface (Fig. 1) rises – but also increases the heat removal according to the rise of the cooling coefficient κ. In order to enable sustained oscillations, these two effects must compensate to such an extent that $a_{11} + a_{22}$ remains positive, but becomes not so strong positive that the catalyst pellet superheats beyong the upper limit of the oscillation field. This condition can be kept by a small range of H_2 partial pressures only, as is shown up by the narrow, sickle-shaped field of oscillations in Fig. 8. At high gas flow rates the convective cooling suppresses the oscillations completely. At lower gas inlet temperatures T_0 the sickle-shaped region is shifted to lower H_2 concentrations.

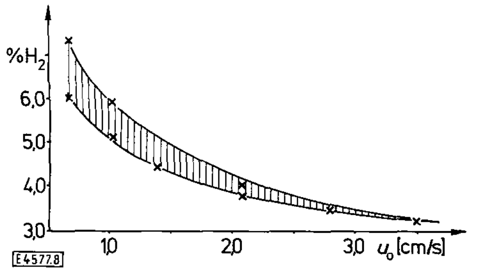

Fig. 8

The region of selfsustained oscillations (hatched) in the diagram % H_2 in air vs. gas flow rate u_0. Gas inlet temperature T_0 = 80 °C [3]

With $a_{11} + a_{22} \approx 0$ an approximate relation for the frequency of the oscillations can be obtained from Eq. (10):

$$\lambda_{1,2} \approx \pm \sqrt{a_{11}^2 + a_{12}a_{21}} = \pm i\omega, \quad \text{or}$$

$$\omega^2 \approx a_{12}(-a_{21}) = (r_{\mathrm{bl}}E_{\mathrm{bl}} - r_{\mathrm{re}}E_{\mathrm{re}})\frac{\Delta T_{\mathrm{a}}}{RT_{\mathrm{s}}^2}\,\frac{r_{\mathrm{s}}}{1-\theta_{0\mathrm{s}}}. \tag{11}$$

The frequency turns out to be proportional to the root of the main reaction rate r_s, it accordingly increases with temperature and with H_2 partial pressure, as was observed.

To sum up it can be stated that the oscillating hydrogen oxidation on a platinum catalyst represents a case where a small and slow side-reaction changes the conditions of the main process and its heat production by affecting reversibly a little part of the catalyst activity, and thereby creates long-periodical oscillations. This is a special example of those oscillations which Frank-Kamenetskii has described [17] as "thermokinetic" ones. It is noteworthy that basic lines of the explanation presented here have been assumed already in the Ph.-D. Thesis of Beusch [7] in 1970. The details of the mechanism of the main process tentatively suggested above as Eqs. (1) to (4), are of minor importance, and this is a bit disappointing from the point of view of reaction kinetics, because it means that the oscillations in this case can not be applied for investigating detailed kinetics of the main process.

3. The Carbon Monoxide Oxidation

3.1. Oscillations and Jumps of Reaction Rate

This reaction represents an example opposite to the foregoing case: The oscillations of the reaction rate on a Pt-alumina supported catalyst are isothermic and narrowly connected with the details of the reaction mechanism. It is not quite easy with a supported catalyst to ensure the con-

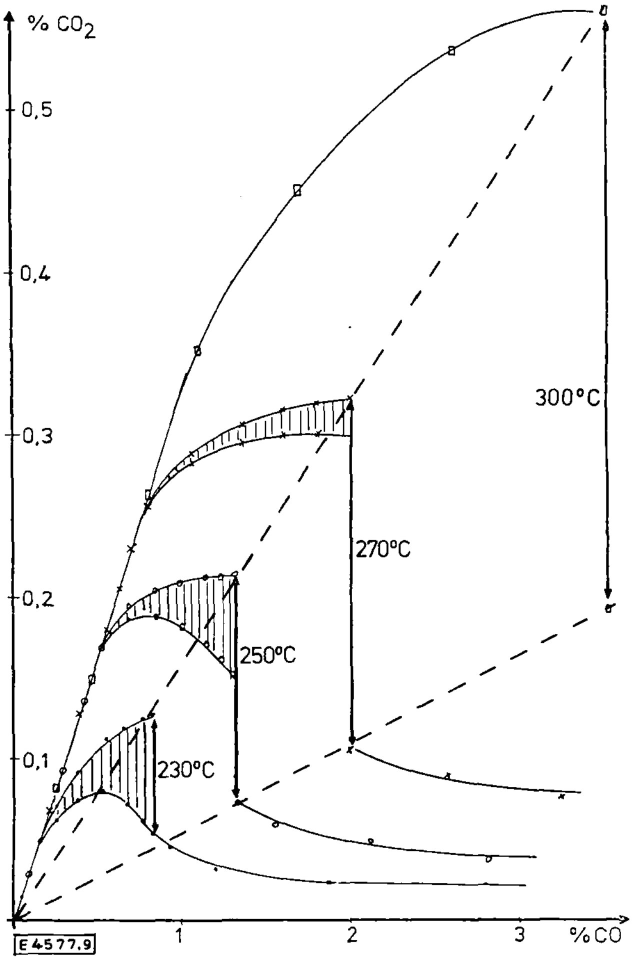

Fig. 9

Reaction rate at different temperatures under isothermal conditions as function of the CO content in mixture with air [4]. Subsidence fields of oscillations hatched. Broken straight lines: connexion of the starting points of quenching and of ignition. (50 mg of pulverized catalyst; 0.1 mm grain size; gas flow rate 20 ml/s) ditions of the purely kinetic case, that is to avoid gradients of temperature and of concentrations. The methods applied to this end and the results obtained are presented in detail elsewhere [18]. The following will be restricted therefore to some main features of the system and to some general conclusions.

Fig. 9 represents the reaction rate (CO_2 percentage in the effluent) as function of the CO content in the incoming gas (air) at different reaction temperatures. The catalyst, pulverized to 0.1 mm particle size, was exposed to the gas flow as a layer of about 1 mm height, and was kept isothermic at the same temperature as the gas flow (for details see [18]). As Fig. 9 shows the system exhibits two steady states with high and with low reaction rates along increasing CO concentrations. The upper state is an oscillatory one; the oscillations – hatched areas – are obviously precursors of the quenching of the reaction rate down to the lower state which is stable for higher CO concentrations. With increasing temperature the oscillations*) gradually vanish; at 300 °C finally the amplitudes are too small and irregular for reliable measurements, but the jumps of quenching and "ignition" still occur (the mark "ignition" for the transition from the lower to the upper stable state will be retained here for favour of brevity, although this ignition is not initiated by heat evolution). It is remarkable that the starting points of quenching as well as of ignition lie on straight lines through the origin in Fig. 9. We will come back to this important observation below.

In order to investigate the changes of state of the catalyst surface during the oscillations, the amount of chemisorbed CO was measured at different phases of an oscillation period. To this end the supply of CO to the incoming air flow was stopped at a certain moment, and the amount of CO_2 was measured in the effluent that occurred from burning off of the CO chemisorbed at the catalyst surface [4, 18]. By means of this method could be demonstrated (Fig. 10) that the oscillations of the reaction rate go along with oscillations of the CO coverage of the surface. One knows since long times that CO inhibits the oxidation reaction on Pt by strong chemisorption, but here arises the problem to understand why the inhibiting CO coverage builts up and is removed periodically during reaction under isothermal conditions. – Beyond this, and coming back to Fig. 9, it should be understood why, besides the alternating type of the CO blocking, a permanent blocking occurs that quenches the reaction, and can be revoked only by lowering the CO partial pressure (or by increasing the temperature) in the lower stable state.

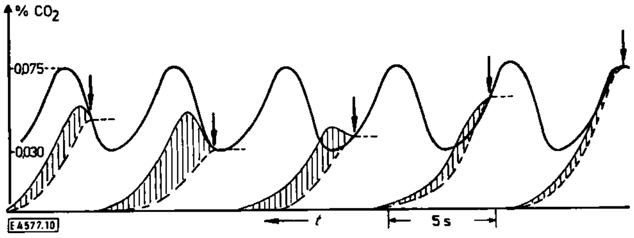

Fig. 10

Amount of CO at the catalyst surface in different stages of the oscillations, represented by the hatched areas between the flushing out curves and the blank runs [4]. Arrows: moment where the stop of the CO supply to the gas flow arrives at the layer of 50 mg catalyst powder. 0.4% CO in air, 205 °C

3.2. The Lines of Quenching and of Ignition

The straight lines in Fig. 9: Reaction rate (r) proportional to p_{CO}, let assume that in this temperature range the thermal desorption of the CO molecules from the Pt surface can be neglected compared with their removal by chemical reaction. The steady-state balance of CO adsorption and removal then reads:

$$r = k_a \cdot \theta_{fr} \cdot \varphi \cdot p_{CO} \tag{12}$$

where k_a is the CO adsorption rate constant, θ_{fr} the fraction of empty adsorption sites, φ the fraction of whole the Pt surface occupied by this type of adsorption sites, and r the reaction rate (CO_2 production). Application of Eq. (12) to the "quenching line" in Fig. 9 means that quenching occurs when the fraction of empty sites, θ_{fr}, drops under a certain critical limit that is represented by the slope of the upper straight line in Fig. 9. The remarkable result that this critical limit is independent of temperature (the other factors, $k_a \cdot \varphi$, in Eq. (12) are practically constant) indicates that the starting conditions of quenching are of statistical nature: CO and O_2 molecules from the gas phase compete for the free adsorption sites, and when the number of these sites approaches a certain lower limit, a small excess of p_{CO} over the balance in Eq. (12) is able to induce the quenching process, in the course of which the Pt surface becomes almost completely covered by CO.

The "ignition line" in Fig. 9 can also be described by Eq. (12) if one assumes that the critical value of θ_{fr} for ignition from the lower stable state is smaller than that for quenching from the upper (by a factor of 3 in Fig. 9). This assumption can be supported by several considerations. The first is that the critical state of the surface at the start of quenching will differ from that at the start of ignition, regarding the structure and geometry of the chemisorbed layers. For instance the critical value of θ_{fr} along the quenching line may relate to coherent surface areas between islands of CO and nuclei of such islands, whereas the critical value of θ_{fr} along the ignition line may consist of single empty sites distributed at random over large areas of CO coverage. – In a second consideration use can be made of the conception of two different types of adsorption sites, α and β, on the Pt surface [18]. The α sites, with lower adsorption energy, are available only for adsorption and surface migration of CO; the β sites, with higher adsorption strength, are those where CO and O_2 compete for, and where the reaction proceeds. Within the scope of this concept the lines of quenching and of ignition could be represented by:

$$r_{qu} = k_a \theta_{fr}^{\alpha} \varphi^{\alpha} \cdot p_{CO}; \qquad r_{ig} = k_a \theta_{fr}^{\beta} \varphi^{\beta} \cdot p_{CO} \tag{13a, b}$$

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*) The oscillation periods observed are between 2 and 10 s, they increase with CO partial pressure and decrease with temperature [18].

respectively. The structure and geometry of the chemisorbed layers in the two critical states will be different, of course, also in this case.

3.3. Possible Mechanisms for CO Clustering and CO Removal

For the descending branches of the oscillations as well as for the quenching process the mechanism of generation and growth of CO islands on the surface — two-dimensional CO clusters — is important. Taking the thermal desorption as negligible, and assuming further that the turnover number of reaction is large also compared to the changes of position of the chemisorbed species by surface diffusion, a possible mechanism for creation and growth of clusters is demonstrated in Fig. 11. Two components A and B may react according to a Langmuir-Hinshelwood mechanism; the tendency to build up clusters then comes from the fact that the reaction removes the pairs AB from the surface whereas the pairs AA (or BB) have a certain chance to grow on to clusters of the pure component A or B, respectively. A member of our group [19] made some computer calculations with this mechanism. He started with a model surface that was covered completely by two components A and B, of 50% each, in random distribution (Fig. 12a). He then simulated reaction steps by choosing AB pairs at random and removing them from the surface; the empty sites were recovered from the gas phase by A or B also at random. After 10000 reaction steps the distribution of the components on the surface had changed appreciably as shown in Fig. 12b, large fields of eather component A or B have formed. Regarding the mechanism of formation, these clusters represent dissipative structures. If one component is favoured, may be by a lower desorption probability, or by a more advantageous distribution of adsorption sites — as is the case with the α and β sites for CO on Pt — the other component will be displaced from the surface after a certain number of reaction steps rather completely*).

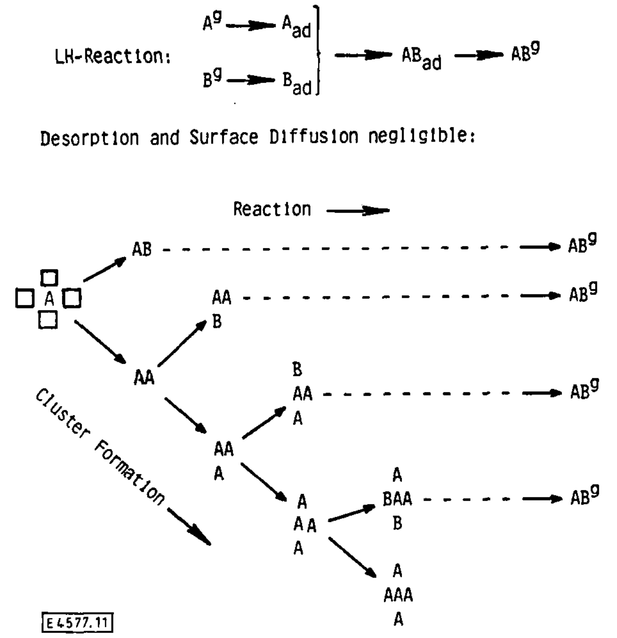

Fig. 11
Scheme of a mechanism for cluster formation and growth as cooperative effect of adsorption and LH-reaction [19]

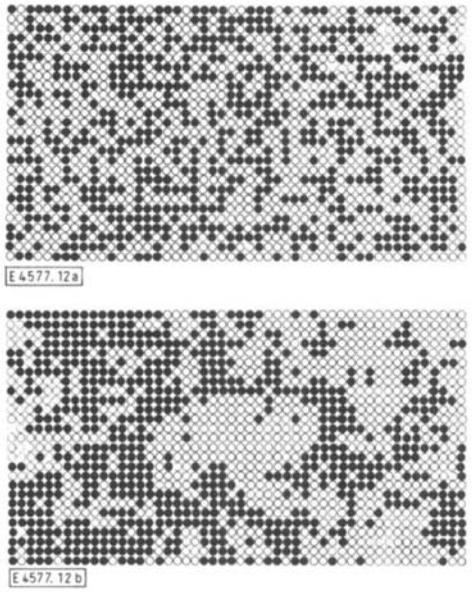

Fig. 12
Development of clusters according to the scheme of Fig. 11 [19].
a) Initial state with random distribution of the two components ● and ○, 50% each.
b) After 10^4 reaction steps, assuming equal adsorption probability of the two components.

It should be mentioned in this context that according to our experience the dispersity of the Pt surface exerts an essential influence. When Angelé [5] studied the oscillations of the CO oxidation at platinized Pt gauzes between 150 and 250 °C in a loop reactor he found an appreciable decrease of catalytic activity with time. This could be attributed, as shown by electron microscopy, to a reconstruction of the highly dispersed crystal agglomeration towards a more smooth structure by rounding off crystal needles, levelling off irregularities a.s.o. The oscillations, indeed, diminished stronger with the aging of the catalyst than the overall activity. — Feldmann [6] working with Pt gauzes in a straight flow reactor at about 200 °C found no unstable behaviour with bright Pt gauzes. Only after coverage with Pt black he could observe jumps of quenching and of ignition; in the high reactivity state — analogous to the oscillation regime in Fig. 9 — statistical fluctuations of the reaction rate occurred, similar to chaotic behaviour. — From these experiences may be concluded that a highly dispersed surface favours the formation of clusters by supplying centers with high adsorption strength (as nuclei), and by impeding surface migration. There is reason to assume that, working with bright Pt wires or foils,

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*) An additional advantage of the CO in this sense is the need for only 1 adsorption site, contrary to 2 neighbouring sites for O_2. As shown earlier with Beusch and Fieguth [10], and confirmed in mathematical modelling by Eigenberger [20, I], this difference is sufficient, principally, to generate quenching and ignition phenomena.

impurities on these surfaces may induce oscillatory behaviour – by heterogenizing the surface and hindering surface migration – whereas the oscillations do no longer occur when the contamination is avoided.

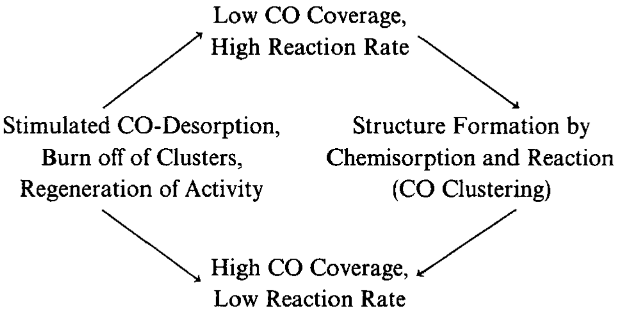
Contrary to the CO oxidation, quenching and ignition phenomena in direct connexion with the oscillations have not been observed in our group for the H_2 oxidation on Pt. Also, no such observations by other workers studying this catalytic system did come to our knowledge. There are jumps of quenching and ignition, of course, as observed by Beusch [7, 9, 10], but these have to be attributed to unstable regions in the co-operation of chemical heat production and convective heat removal. In the upper state, accordingly, the reaction runs in the heat transfer regime with rates practically independent of temperature. Oxygen, indeed, seems not to be able to block up the catalytic activity of the Pt surface so suddenly and completely as is done by CO when it quenches the reaction.

Besides the self-impediment of the reaction by building up CO clusters at the catalyst surface we finally need a regeneration process that provides for a recovery of the reaction rate in the oscillation minima and in the quenched state. As one knows from calorimetric and equilibrium measurements as well as from infrared spectroscopy the energy of chemisorption of CO on Pt decreases with increasing density of packing in the surface. This effect, besides regarding energetic heterogeneities of the surface, can be attributed to the competition of the CO molecules for the electrons of the transition metal (back-bonding [21]), and acts strongest, therefore, on the next neighbours. Accordingly, the desorption probability of a CO molecule is higher out of a cluster than from an isolated position on the surface. With increasing cluster growth along the falling off branches of reaction rate the probability of CO desorption out of the clusters increases up to a maximum value. This opens chemisorption sites for oxygen from the gas phase, and initiates the burning off of the CO clusters from the catalyst surface, whereby the reaction rate becomes regenerated. If the CO/O_2-ratio in the gas phase is above the critical limit, however, the chemisorption sites emptied in the CO clusters will be recovered so largely by CO that no regeneration occurs, but the reaction rate from the oscillation minimum falls down further to the lower stable state, i. e. the reaction becomes quenched. – In this process a buffer mechanism as conceived by Eigenberger [20, 11], exerted by a non-reactive chemisorption species of CO (for instance the α-CO mentioned above) may also be involved.

The dependence of activation energies of surface processes on coverage has been considered repeatedly as the reason for oscillatory behaviour, especially in the case of catalytic oxidation of H_2 and of CO [22 – 25], but it was the activation energy of the reaction itself – not of a desorption process – that was taken linearly dependent on coverage. Whereas by means of this assumption oscillations can be created generally in mathematical modelling, difficulties arise to explain the rather long periods observed [22], and in the case of CO oxidation to represent the jumps of quenching and ignition. For obtaining longer periods additional chemisorbed species – or even dissolved species – are assumed [2] which lengthen the relaxation time by their storage capacity without participating in the reaction. – McCarthy et al. [26], on the other hand, tried to explain the observed oscillations during CO oxidation on a $Pt-Al_2O_3$ carrier catalyst by means of an assumed transition from an Eley-Rideal mechanism to a Langmuir-Hinshelwood mechanism in the region of maximum reaction rate where the oscillations occur. Besides considering recent experimental results [27, 28], according to which an ER mechanism of the CO oxidation on Pt and Pd appears rather improbable, this conception also does not cover the quenching and ignition phenomena.

3.4. Conclusions

Summarizing our conclusions from whole the experimental evidence we present the following qualitative scheme of the cycling surface processes in the unstable region of the CO oxidation on platinum:



Low CO Coverage,
High Reaction Rate

Structure Formation by
Chemisorption and Reaction
(CO Clustering)

High CO Coverage,
Low Reaction Rate

Stimulated CO-Desorption,
Burn off of Clusters,
Regeneration of Activity

The competitive processes: CO clustering and stimulated CO desorption followed by regeneration of the reaction rate are analogous to the blocking and reactivation processes in the case of hydrogen oxidation. When one attempts to set up the balance equations with these two processes for the CO and the oxygen coverage of the surface, however, one runs into the problem that no expression for the reaction rate is available which considers a non-random distribution of the components on the surface, as it is represented, for instance, in Fig. 12b. The LH-expression is not applicable, because it is based on random distributions and does not take into account clustering. A new and basic problem arises here, the handling and modelling of which must still be developed.

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E 4577

Stability Phenomena in Chemical Reactors

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Aktiver Transportprozeß / Mehrfache stationäre Zustände / Oszillationen / Reaktionszone / Stabilität

Some important types of non-linear phenomena occuring in chemically reacting systems are explained by means of some single examples of chemical reactors. Multiple steady-states exhibiting a distinct behavior of ignition and extinction are in the category of these phenomena. In addition all dynamic instabilities, of which there are a wide variety must also be included. These instabilities might be of thermal or purely kinetic nature, or they may result from the interaction of chemical reaction and physical transport processes. Generally these instabilities result in increasing oscillations which finally converge in stable limit cycles. The moving reaction zone which can appear in fixed-bed reactors is described in greater detail in order to demonstrate that such a dissipative structure may be considered a prototype of an active transport process. This kind of active transport process can be observed in many systems, which are not limited just to chemical engineering. Furthermore, it is emphasized that a moving reaction zone is characterized by a certain feature which here is called "form stability". This property might be used in order to considerably reduce the order of the non-linear equations, describing the reactor behavior. Model reduction is of great importance with respect to both a detailed analysis of the dynamic behavior of a reactor and to the design of control concepts.

Introduction

It is the intention to present a short survey of some characteristic stability phenomena occurring in chemical reactors. This paper will be limited, in that we shall give only a physical interpretation of these appearances. We are not going to treat mathematical methods for the solution of stability problems in chemical reactors. For further information concerning such mathematical methods, we refer to a number of survey papers given, for example, by Schmitz, Ray and others [1 – 7].

It is well-known that the dynamic behavior of chemical reactors is determined by the interaction of chemical reactions and physical transport processes, such as heat conduction, diffusion and convection. Often the non-linear dependencies of the reaction rate, with respect to temperature, pressure, and concentrations, have an essential influence upon the dynamic properties of a reactor. This means that a wide variety of phenomena characteristic to non-linear systems can be observed in chemical reactors.

Multiple steady-states exhibiting a behavior of ignition and extinction are in the category of these phenomena. In addition, all dynamic instabilities which might be of thermal or of purely kinetic nature, must also be included. The moving reaction zone is another interesting phenomenon which can appear in fixed-bed reactors.

We are now going to explain these phenomena by means of some simple examples of chemical reactors. The moving reaction zone will be described in greater detail, in order to demonstrate that this appearance may be considered a prototype of an active transport process. Furthermore, it will be emphasized that a moving reaction zone is characterized by a certain feature, which here is called "form stability". This property might be used in order to considerably reduce the order of the non-linear equations.

Multiple Steady-States

The continuous-stirred-tank-reactor (CSTR), has enjoyed great popularity in system analysis (Fig. 1). This is due not only to its importance in chemical engineering, but also because of the simplicity of the describing equations. Owing to its continuous mass flow, the CSTR reactor is found to be in both heat- and mass-exchange with its surroundings, and hence represents an open thermodynamic system. Assuming a complete mixing of the reactants within the reactor, local temperature and concentration gradients need not be taken into account.

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