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Formation of Turing structures in catalytic surface reactions: The facetting of Pt(110) in CO + O₂

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The Pt(110) surface facets during the catalytic oxidation of CO, if reaction conditions are adjusted such that the CO-induced $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition can take place simultaneously. A detailed low-energy electron diffraction beam profile analysis revealed that regularly spaced (430) and (340) facets are formed with a lateral periodicity of ~ 70 lattice units along the $[1\bar{1}0]$ direction. This result, together with the observation that the faceted surface is only stable under reaction conditions, indicates a dissipative structure of the Turing type. Such structures, which are stationary but exhibit a periodic variation of the concentration variables in space, have so far almost exclusively been discussed theoretically. The interpretation of the faceted surface as a Turing structure could be confirmed by a Monte Carlo simulation based on the Langmuir Hinshelwood mechanism of catalytic CO oxidation and the CO-induced $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition.

I. INTRODUCTION

In open systems which are far from thermodynamical, equilibrium new phenomena can be observed that are not permitted in a closed system at thermodynamical equilibrium.¹ Typical examples are kinetic oscillations and/or chemical waves. Besides such time-dependent phenomena one may also observe another type of nonequilibrium structure which is stationary but exhibits a periodic modulation of the concentration variables in space. These structures are known in the literature as Turing structures after A. M. Turing who first discussed them in 1952 as a theoretical model for morphogenesis.^{2,3} The basic idea of this model was that spontaneous spatial pattern formation may occur in a reaction diffusion system, if the homogeneous state is unstable with respect to a perturbation by diffusion.

Although Turing structures have been discussed quite often in theoretical publications, so far only one clear-cut experimental realization could be achieved in fluid phase reaction systems.³ Possible candidates are the reaction systems which exhibit kinetic oscillations such as the famous Belousov-Zhabotinskii reaction. The reason for the difficulty in detecting Turing structures in homogeneous reaction systems is quite evident. Since a Turing instability requires strongly different diffusion constants of the reactants, the chances are rather slim of finding one in fluid phase, where most substances diffuse about equally fast.⁴

Next we consider the chances for detecting Turing structures in heterogeneous catalysis, in particular in the case of the catalytic oxidation of CO on Pt surfaces. On surfaces the diffusion constants are known to vary considerably for different adsorbates. So adsorbed CO diffuses rather rapidly on Pt surfaces whereas the more tightly bound oxygen is almost completely immobile at lower temperatures ($T < 600$ K). Besides the diffusion of CO_{ad} and O_{ad} one also has to take into account the diffusion of Pt atoms which may alter the surface structure and can thus modify the reactivity of the surface. Candidates for the formation of Turing structures are systems which exhibit kinetic oscillations such as Pt(100)/CO + O₂ and Pt(110)/CO + O₂. Kinetic oscilla-

tions exist there as a consequence of adsorbate-induced surface phase transitions which modify the catalytic activity, namely the $1 \times 1 \rightleftharpoons \text{hex}$ phase transition of Pt(100) and the corresponding $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition of Pt(110).^{5,6} It turned out that the faceted surface which is formed during catalytic CO oxidation on Pt(110) can indeed be classified as a structure of the Turing type. Experimental evidence for this interpretation is presented in this report. In addition we could reproduce the experimental results by a Monte Carlo simulation solely based on the known elementary steps of the surface reaction and the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition.

II. CHARACTERIZATION OF THE FACETTED Pt(110) SURFACE

A facetting of Pt(110) during catalytic CO oxidation was detected in the 10^{-4} Torr range when reaction conditions were adjusted to those where the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition also proceeds.^{7,8} Almost exclusively facets belonging to the [001] zone were formed. These gave rise to a unidirectional splitting of the integral order beams along the $[1\bar{1}0]$ direction in low-energy electron diffraction (LEED). The facets were quite small, of the order of ~ 100 Å, and could be easily removed by heating the sample above ~ 500 K. The facetting of a surface due to the interaction with a strong adsorbate is not unusual. In the present case, however, several observations contradicted the idea of a simple adsorbate-induced restructuring of the surface.

Firstly, a facetting of Pt(110) was only observed under reaction conditions but not with one of the gases alone. Secondly, a thermal reordering process slowly restores the flat (110) surface after stopping the flow of CO and O₂. This demonstrates that the faceted Pt(110) surface is thermally unstable. Finally, the existence of kinetic oscillations in the same system under similar conditions (at higher T) suggests a decisive role of kinetic instabilities in the facetting process itself.⁸ All these observations demonstrate that the faceted surface is stable only under reaction conditions and thus belongs to the class of so-called "dissipative structures."¹ The

classification of the faceted surface as a dissipative structure of the Turing type was finally substantiated by the results of a detailed LEED beam profile analysis (SPALEED).⁹ The measurements carried out with a high-resolution instrument of $\sim 2000 \text{ \AA}$ transfer width revealed that the facets on Pt(110) exhibit in fact a lateral periodicity as is required for a Turing structure.

The results of profile measurements of the 0,0 beam in the $[1\bar{1}0]$ direction are displayed in Fig. 1. The beam energy had been varied there close to in-phase scattering conditions for different vertical terrace layers of Pt(110). This condition is reflected by the vertical scattering phase S which relates to the vertical component K_1 of the scattering vector and the vertical layer distance d via $S = K_1 d / 2\pi$. One notes that first- and second-order satellites appear as one moves away from the Bragg energy ($S = 2.0$) and that the satellite splitting remains constant as the energy is varied. The formation of higher-order satellites indicates that a regularly spaced array of facets exists on the surface. This periodicity taken together with the orientation of the facets, which can be determined from the spot splitting at out-of-phase scattering conditions ($S = 2.5$), leads to a simple geometric model of the faceted surface. This is displayed in the inset of Fig. 1.

A symmetric sawtooth-like array of alternating (340) and (430) orientations builds up a regular structure characterized by a lateral periodicity of 200 \AA (74 lattice units) along the $[1\bar{1}0]$ direction. A ball model of a (430) facet showing the structural elements of (110) terraces and (100) steps that build up the surface of the (430) facet is displayed in Fig. 2. A comparison between the measured intensity pattern of the satellites and the intensity distribution calculated from the geometrical model shows good agreement as evidenced by Fig. 1. The calculation of the profiles was carried out for the case of an ideal periodic structure. On the real surface, however, structural disorder is also present. Therefore the agreement between theoretical and measured profiles is only good close to in-phase scattering conditions (up to $S \sim 2.10$), while the contribution of structural disorder

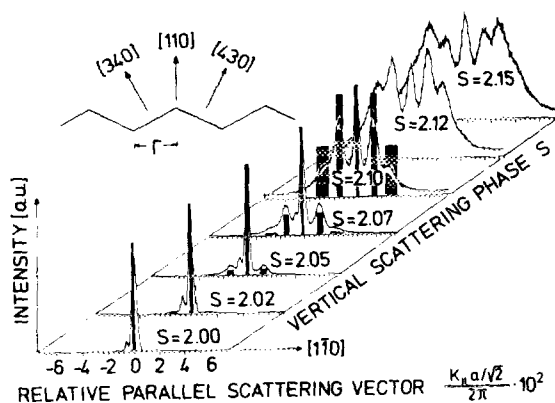


FIG. 1. Comparison between the measured spot profiles and the profiles calculated from the geometrical model of the faceted surface displayed in the inset. 2Γ denotes the lateral periodicity of 74 lattice units along the $[1\bar{1}0]$ direction found in the experiment. For better visual comparability the width of the columns is changed simultaneously with the width of the measured spots.

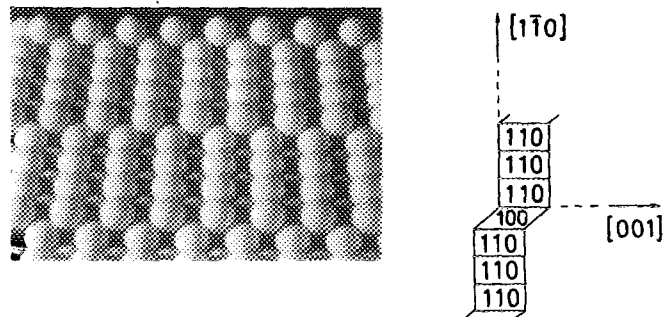


FIG. 2. Ball model of the (430) facet illustrating the structural elements of nonreconstructed (110) terrace units and (100) step units that represent the facet.

becomes significant for larger deviations. The important result of the profile analysis is that the faceting of Pt(110) in $\text{CO} + \text{O}_2$ leads to the development of a well-defined lateral periodicity. The faceted surface thus represents an example for spatial pattern formation in a reaction-diffusion system similar to other nonequilibrium systems in physics.¹

III. CONDITIONS FOR FACETTING

The faceting of Pt(110) during catalytic CO oxidation has been extensively studied in the 10^{-4} Torr range at temperatures between ~ 400 and 530 K .⁷⁻⁹ The conditions for faceting and the changes in catalytic activity caused by faceting can be conveniently summarized in a plot of the reaction rate r_{CO} vs p_{CO} as displayed in Fig. 3. In principle the kinetics of catalytic CO oxidation exhibit two different branches characteristic of the Langmuir-Hinshelwood (LH) mechanism along which the reaction proceeds. At low

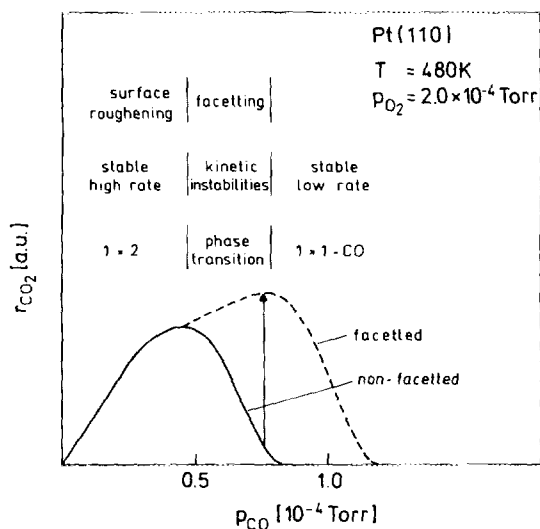


FIG. 3. Relation between the conditions for faceting and the kinetics of the catalytic CO oxidation on Pt(110). The full line indicates the rate curve for the nonfaceted surface, while the dashed curve indicates the increase in catalytic activity after strong faceting of the surface. The different regions indicated on top of the rate curve all refer to the nonfaceted Pt(110) surface.

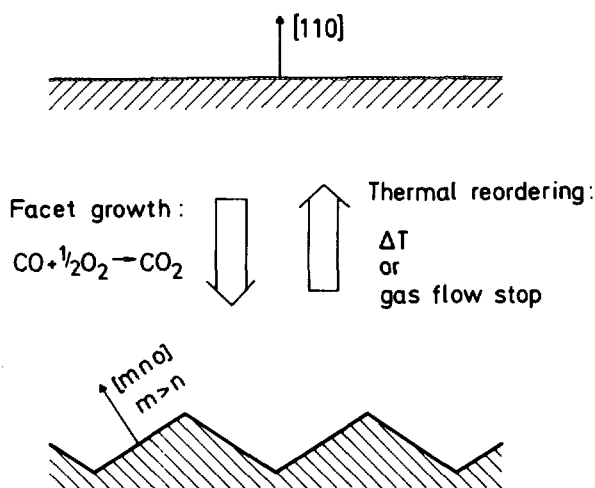


FIG. 4. Schematic diagram illustrating the faceting process as a dynamical equilibrium between reaction-induced growth of facets and thermal annealing.

p_{CO} an oxygen-covered 1×2 surface exhibits a high reactivity, but with increasing p_{CO} the rate finally jumps from the high rate branch to a state with a low activity. On this low rate branch a high CO coverage inhibits oxygen adsorption and hence the surface reaction.

The faceting of Pt(110) was found to be restricted to the transition range between the two branches of LH kinetics which is the region where the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition proceeds. In the same range one may also observe kinetic oscillations, under appropriate conditions, which arise due to the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition.^{8,10} In the faceting process, however, the reaction rate does not oscillate, but it increases monotonously until the higher rate branch is reached as it is indicated by the arrow in Fig. 3. The rate maximum of the faceted surface is shifted towards higher p_{CO} values with respect to the unfaceted surface thus signalling an increase in catalytic activity. Quite remarkably the position of the new rate maximum is located just at the end point of the arrow in Fig. 3 marking the increase in the reaction rate for a given p_{CO} . This behavior demonstrates that the surface facets only to the extent which is necessary to reach the high rate branch.

Subsequent adsorption experiments demonstrated that the increase in catalytic activity is due to a higher oxygen sticking coefficient s_{O_2} on the faceted surface.⁷ The origin of this difference could be traced back to the formation of (100) steps in the faceting process. These exhibit a higher s_{O_2} than do flat (110) terraces and consequently s_{O_2} will rise together with the degree of faceting. As will be shown in a Monte Carlo simulation presented in the following section, it is in fact the increase in s_{O_2} which directs the structural changes towards the development of regular facets.

As was observed experimentally, a thermal reordering process slowly restores the flat (110) surface as soon as the surface reaction ceases. Since a thermal reordering process will also exist under conditions of facet growth, the amount of faceting that can be achieved for given conditions will be

determined by a dynamical balance between two competing processes as is depicted in Fig. 4. The competition between reaction-induced growth of facets and thermal reordering has the consequence that a (pressure dependent) high temperature limit exists for the faceting of Pt(110) in $\text{CO} + \text{O}_2$. While an increase in temperature can strongly enhance the thermal mobility of Pt atoms, the rate of facet growth being proportional to the reaction rate will be limited by the partial pressures. The existence of an upper temperature limit at $T = 530 \text{ K}$ for faceting is demonstrated for $p_{\text{O}_2} = 1.5 \times 10^{-4} \text{ Torr}$ in Fig. 5. In this diagram the shift in the position of the rate maximum Δp_{CO}^* and the splitting δ_F of the integral order beams in LEED served to monitor the degree of faceting.¹¹

IV. SIMULATION OF THE FACETTING PROCESS

The elementary step in the faceting of Pt(110) is clearly the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition. This can be easily shown with a ball model. The mass transport of 50% of the surface atoms associated with the phase transition necessarily creates steps. By arranging (100) steps and (110) terrace units in a regular sequence it is possible to build up all orientations of the [001] zone. How this simple mechanism can cause the formation of regular facets has been demonstrated in a Monte Carlo simulation, in which we tried to mimic the

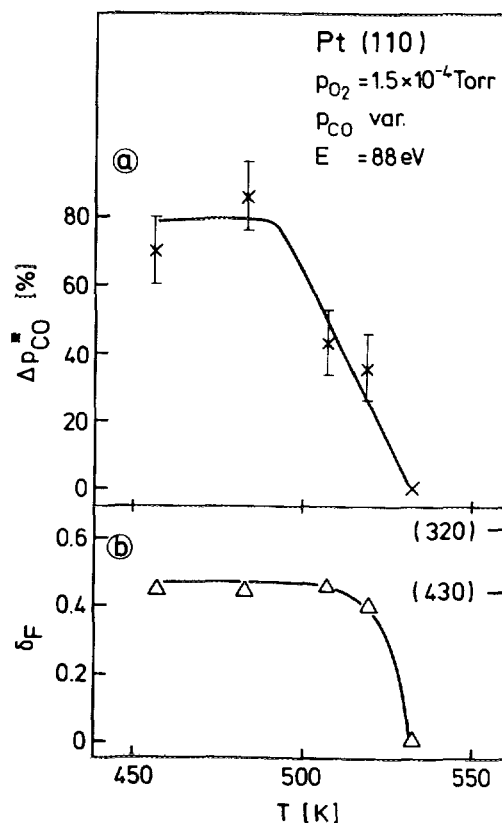


FIG. 5. Maximum degree of faceting that could be reached at different temperatures for fixed $p_{\text{O}_2} = 1.5 \times 10^{-4} \text{ Torr}$ and with varying p_{CO} . The splitting δ_F (normalized with respect to the \mathbf{a}^* reciprocal lattice vector) of the integral order beams in LEED and the shift in the position of the rate maximum Δp_{CO}^* served to indicate the degree of faceting. (After Ref. 10.)

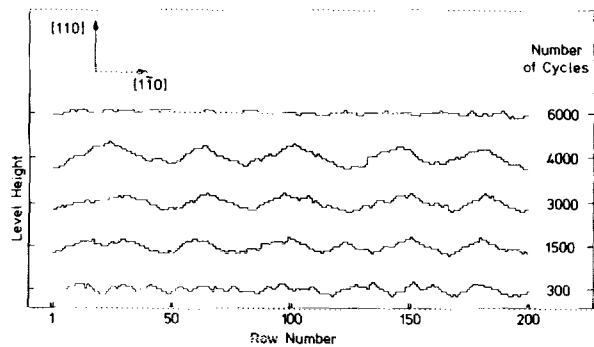


FIG. 6. Monte Carlo simulation showing the development of a regular facet structure during the catalytic CO oxidation on Pt(110) followed by a restoration of the flat surface after stopping the gas flow at 4000 cycles. (After Ref. 12.)

diffusion of Pt atoms under the influence of catalytic CO oxidation.¹² This simulation was based solely on the known properties of the CO-induced $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition and on the elementary steps of the LH mechanism by which the catalytic oxidation of CO proceeds. In addition the oxygen sticking coefficient s_{O_2} has been made dependent of the local surface structure by setting s_{O_2} twice as high for (100) step sites than for (110) terrace sites.

As demonstrated with a ball model the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition can either create or annihilate (100) steps following the rule of mass conservation. In order to simplify the complexity of the problem, the possible movements of Pt atoms were restricted to diffusion along the $[1\bar{1}0]$ direction. This appears to be justified since faceting in the experiment was also found to be restricted along this direction. The results of a simulation in which the Pt(110) surface was exposed to a constant flow of CO and O_2 comparable to the experimental conditions are displayed in Fig. 6. One notes that the initially flat surface roughens as a result of local CO coverage fluctuations. These cause the mass transport of Pt atoms to occur every time the surface undergoes the phase transition. As the reaction proceeds, one observes the formation of a regular facet structure which remains stationary beyond ~ 4000 cycles. In order to demonstrate that the faceting is in fact due to the ongoing surface reaction and not caused by a hidden thermodynamic stabilization, the flow of the gases was stopped after 4000 cycles. The thermal reordering process which is then dominant alone leads to the restoration of the flat Pt(110) surface, as it is demonstrated by the profile recorded after 6000 cycles.

The simulation described above could reproduce practically all essential features of the experiment. The lateral periodicity of 40 lattice units in $[1\bar{1}0]$ direction is not very far from the experimental value of ~ 70 lattice units. Even the time scale is comparable since the 4000 cycles in the simulation correspond to ~ 400 s in real time, which is roughly the period during which faceting develops in the experiment. In addition the simulation could also correctly reproduce the region in p_{CO} parameter space where faceting occurs and the increase in catalytic activity.¹² The simulation thus confirms the interpretation of the faceted Pt(110) surface as a

Turing structure, and it provides a detailed microscopic picture of how the interplay between the LH reaction and the phase transition can give rise to a faceting process.

The faceting of a surface either caused by an adsorbate or by lack of thermodynamic stability of the clean surface has been observed quite often in experiments.¹³ In these cases the behavior of the surface is usually governed by equilibrium thermodynamics leading to the formation of more stable orientations. Quite differently the faceting observed here causes the formation of very open and reactive surfaces which are thermally unstable. This is the principle difference between faceting as a dissipative structure as it is observed here and faceting controlled by equilibrium thermodynamics. For obvious reasons this difference is quite relevant for heterogeneous catalysis where reactive surface configurations might exist as dissipative structures under reaction conditions.

V. CONCLUSIONS

The Pt(110) surface facets under the influence of catalytic CO oxidation, if reaction conditions are adjusted such that the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition can proceed simultaneously. A detailed LEED beam profile analysis demonstrated that the faceted Pt(110) surface exhibits a periodic structure in which facets of uniform orientation and size build up a symmetric sawtooth-like array. The faceted surface is characterized by a lateral periodicity of ~ 70 lattice units along the $[1\bar{1}0]$ direction. This structure was interpreted as a Turing structure which develops because the flat surface is unstable against the diffusion of Pt atoms under reaction conditions. This interpretation could be confirmed in a Monte Carlo simulation based on the LH mechanism of catalytic CO oxidation and on the $1 \times 1 \rightleftharpoons 1 \times 2$ phase transition. The faceting of Pt(110) in $CO + O_2$ thus represents one of the very few examples where a Turing structure has been found in experiment.

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