Homogeneous and Heterogeneous Front Nucleation in a Bistable Surface Reaction: The NO + CO Reaction on a Cylindrical Pt Crystal

G. Vesser  
*Fritz-Haber-Institut der Max-Planck-Gesellschaft*

Patricia A. Thiel  
*The Ames Laboratory (U.S. Department of Energy) and Iowa State University, thiel@ameslab.gov*

R. Imbihl  
*Fritz-Haber-Institut der Max-Planck-Gesellschaft*

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Abstract
Under continuous flow conditions the oscillatory NO + CO reaction on Pt(100) exhibits bistability in the temperature range below 440 K. In this range, an inactive stationary branch coexists with a reactive oscillatory branch. The transition from the inactive branch, which is only metastable, to the truly stable active branch proceeds via propagating reaction fronts. The associated nucleation process has been investigated in the 10^{-6} mbar range using photoemission electron microscopy (PEEM) as a spatially resolving method. A Pt sample of cylindrical shape whose surface comprises the highly active orientational range between (100) and (3 10) was used as a catalyst. Depending on the degree of supersaturation, both heterogeneous and homogeneous nucleation have been found. Homogeneous nucleation manifests itself in the occurrence of a so-called "surface explosion" at \( T_c = 440 \) K. Below this temperature, heterogeneous nucleation occurs. Depending on the preparation of the inactive state, we observe two different nucleation scenarios which we can tentatively assign to two different kinds of defects.

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G. Veser, P. A. Thiel,* and R. Imbihl
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

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Under continuous flow conditions the oscillatory NO + CO reaction on Pt(100) exhibits bistability in the temperature range below 440 K. In this range, an inactive stationary branch coexists with a reactive oscillatory branch. The transition from the inactive branch, which is only metastable, to the truly stable active branch proceeds via propagating reaction fronts. The associated nucleation process has been investigated in the 10^{-6} mbar range using photoemission electron microscopy (PEEM) as a spatially resolving method. A Pt sample of cylindrical shape whose surface comprises the highly active orientational range between (100) and (310) was used as a catalyst. Depending on the degree of supersaturation, both heterogeneous and homogeneous nucleation have been found. Homogeneous nucleation manifests itself in the occurrence of a so-called "surface explosion" at Tc = 440 K. Below this temperature, heterogeneous nucleation occurs. Depending on the preparation of the inactive state, we observe two different nucleation scenarios which we can tentatively assign to two different kinds of defects.

Introduction

The NO + CO reaction has been shown to exhibit rate multiplicity, oscillatory behavior, and spatial pattern formation on a Pt(100) surface.1,2 Propagating reaction fronts, spiral waves, and turbulent patterns have been observed at temperatures between about 420 and 440 K.3-5 In this parameter range the surface reaction rate oscillates only on a local scale, but macroscopic rate oscillations can be excited by a small synchronizing T-jump. These oscillations then damp out within a few oscillation periods. In this paper, we report on the nucleation and propagation of reaction fronts in this temperature region, where a reactive oscillatory state coexists with an unreactive state, thus giving rise to a bistable region. The nucleation of the more stable phase depends on the way the experiment is conducted; in our experiments we observe both homogeneous and heterogeneous nucleation processes similar to equilibrium phase transitions. As will be shown, structural defects play a dominant role in the nucleation of reaction fronts, but if the experiment is conducted in such a way that a high degree of supersaturation is reached, homogeneous nucleation can be observed. Moreover, we also observe two different scenarios in heterogeneous nucleation which we tentatively attribute to two different structural defects on the surface. Which type becomes active depends on the history of the reaction system and on the reaction conditions.

The investigation was conducted using a Pt single crystal of cylindrical shape as a catalyst with the cylinder axis being aligned parallel to the [001] direction. The catalyst surface therefore comprises all orientations of the [001] zone. Due to this inherent structural heterogeneity, the nucleation and propagation of reaction fronts are to a large degree determined by structural defects, i.e. by a continuously varying step density on the cylinder surface. Previous investigations with the same cylindrical crystal have already shown that the NO + CO reaction is very structure sensitive since only an orientational range extending from (100) to roughly (310) displayed oscillatory behavior.3,4 In addition, one observes that the spatial pattern formation in this reaction is strongly influenced by structural defects which, for example, can determine the path of a propagating reaction front. This dependence can be traced back to the well-known structural sensitivity of NO dissociation on Pt surfaces.6-8

Experimental Section

The experiments were conducted in a standard UHV chamber (volume ≈ 80 L), which under reaction conditions was operated as a gradient-free flow reactor (effective pumping rate ≈ 100 L/s).1 Apart from the usual UHV equipment for cleaning the sample and testing sample cleanliness, the chamber was equipped with a photoemission electron microscope (PEEM) for spatially resolving investigations.9 This method is based on the photoeffect, as the sample is illuminated with UV light from a deuterium discharge lamp. The yield of the ejected electrons is strongly dependent on the local work function of the crystal, which is altered locally by the adsorption of gases. Collecting the ejected photoelectrons and focusing them by means of a three-lens electron optics onto a phosphorus screen allows PEEM to be used therefore as an in situ method to obtain an image of the locally varying adsorbate coverage with high spatial (typically 1 μm) and temporal (20 ms) resolution. In the PEEM images one can essentially distinguish between bright areas associated with either a large NO coverage or a mostly adsorbate-free surface area, and therefore a correspondingly high reactivity, and dark areas characterized by a large CO coverage and low reactivity.4 Parallel to PEEM, measurements of the reaction rate were performed with a differentially pumped quadrupole mass spectrometer (QMS). The platinum cylinder (inner diameter 10 mm, outer diameter 17 mm) has already been characterized in earlier investigations with respect to structure and reactivity.3 On the Pt cylinder, an orientational range extending roughly from (100) to (310) is very active in the NO + CO reaction and only this range was found to exhibit local oscillations and spatial pattern formation.2 Accordingly, we will restrict ourselves entirely to this range in the present report.

Results and Discussion

Figure 1 displays the two branches of the reaction rate, as they can be obtained by slowly heating and cooling the sample in a mixed NO/CO atmosphere with fixed pNO and pCO.1,2 Starting at low temperature and slowly heating the sample, the system stays on the unreactive branch characterized by a high adsorbate coverage which inhibits NO dissociation and hence the
overall reaction. At a critical temperature, \( T_c \), of about 440 K, the system undergoes a steep transition to the active branch of the rate hysteresis, characterized by a low adsorbate coverage and a correspondingly high reaction rate. This transition is accompanied by a pronounced overshooting of the reaction rate, which marks the so-called "surface explosion," i.e., the vehement autocatalytic reaction of the adsorbates on the surface. As the temperature is lowered from this point, the system remains on the reactive branch; until close to 420 K, the inactive state is reestablished by the increasing adsorbate coverage on the surface. In the following we will focus entirely on the bistable temperature region between the two described transition points, i.e., the two hysteresis branches below the "surface explosion" temperature.

In the temperature range below the "surface explosion" region, the system is not truly bistable between 433 and 440 K, but the hysteresis arises due to kinetic effects in this region. When the heating procedure is terminated somewhere on the inactive branch above 433 K, a transition from the low-rate to the high-rate branch takes place via nucleation and propagation of reaction fronts. This transition process from the inactive to the active branch proceeds very slowly; i.e., complete conversion takes place typically within 20-30 min. The metastability has gone unnoticed in earlier investigations and can be attributed to the presence of atomic steps running parallel to the orientation of the cylinder axis.

The nucleation process depends on the way the inactive surface is prepared before the nucleation. The observations on a local scale are as follows. As an adsorbate-covered surface is slowly heated at the surface in a mixed NO/CO atmosphere to about 433 K, a couple of reactive islands nucleate at some macroscopic defects (diameters \( \approx 5-20 \mu m \)) on the surface. This process is shown in the PEEM image of Figure 2a, where one can clearly make out the defect that nucleates the reaction front. The elliptical shape of the front indicates the strong anisotropy of the front propagation velocity. While the propagation velocity in the [001] direction (i.e., in the direction of the cylinder axis) is about 14 \( \mu m/s \), one can estimate from the ratio of the diameters of the ellipse that the velocity perpendicular to it is about 1 order of magnitude smaller (measured value \( \approx 2 \mu m/s \)). The anisotropy has already been noticed in earlier investigations and can be attributed to the presence of atomic steps running parallel to the orientation of the cylinder axis.

As one increases the temperature further, no acceleration of the propagation velocity can be measured with the experimental accuracy of \( \approx 10\% \). At the temperature of the "surface explosion," i.e., at \( T_c = 440 \) K, reaction fronts nucleate all over the remaining inactive surface and conversion takes place so rapidly that individual reaction fronts can no longer be discerned. The overshooting of the global reaction rate that marks the "surface explosion" is then proportional to this remaining area.

Foremost, these observations suggest that on an ideal, defect-free surface, the hysteresis would be truly bistable. The formation of reaction fronts below \( T_c \) can clearly be attributed to heterogeneous nucleation. Quite in contrast, we can associate the rapid nucleation process to homogeneous nucleation. The occurrence of a "surface explosion" can be seen as analogous to the well-known superheating of liquids or supersaturation of liquid solutions; the nuclei spontaneously form all over the remaining inactive area, thus causing a very rapid transition to the stable state. It is well-known from nucleation theory that the rate of homogeneous nucleation strongly increases with the differences in free enthalpy between the two phases. The nucleation rate therefore becomes very fast if a high degree of supersaturation is achieved, which is apparently the case in the "surface explosion".

In the following, we examine more closely the temperature range below \( T_c \) in which heterogeneous nucleation was observed. Cooling to sufficiently low temperatures (\( T \leq 420 \) K) in repeated experiments revealed identical scenarios with the reaction fronts always nucleating at the same defects. If, however, one stops the cooling at temperatures slightly above the threshold temperature of \( \approx 420 \) K, the nucleation process changes drastically. As demonstrated in the PEEM image in Figure 2b, many reaction fronts develop simultaneously all over the surface upon heating the sample above 436 K again. In contrast to the case in previous experiments, no defects can be made out which could act as nuclei for the reaction fronts.

Repeated temperature cycling experiments demonstrated a distinct behavior for the two different types of nucleation below \( T_c \); in the first type of experiment, reaction fronts always nucleate at the same few macroscopic defects while, in the second type of experiments, the reaction fronts nucleate in different numbers and at different places. Additionally, the temperature at which they appear is somewhat higher than the temperature of the unambiguously heterogeneous nucleated fronts (436 K vs 433 K). At first glance, these observations would indicate that the reaction fronts in the second type of experiment are indeed homogeneously nucleated, because heterogeneous nucleation due to surface defects should always take place at the same places in repeated experiments. However, such an assignment is premature...
since a number of experimental observations, which will be presented below, point toward another explanation.

Some time after the nucleation, the individual reaction fronts merge and form a single large reaction front which is oriented parallel to the cylinder axis due to the anisotropic propagation velocity. This large reaction front always nucleates around (1010), which is the most active orientation. From there it slowly propagates toward the less reactive orientations. During this propagation, one can sometimes make out a kind of "prenucleation"; i.e., a reaction front nucleus forms on the inactive surface shortly before the reaction front actually reaches this area. An example of this process is shown in the PEEM image in Figure 3a, where one can see a small reactive island that nucleated some 20 μm in front of the main reaction front. Since no reactive paths (i.e., bright lines) that could connect the small reactive island with the main front are visible in PEEM, the interpretation of this effect is unclear at first sight. One possible explanation could be that a concentration gradient accompanying the main reaction fronts reaches far enough into the unreactive part of the surface to trigger the formation of secondary reaction fronts, but intensity profiles of the PEEM images do not show such an effect.

The explanation that appears to be most likely comes up as one follows the further development of the front behavior depicted in Figure 3. One can see that, during the growth of the prenucleated reactive island, it becomes strongly elongated toward the main reaction front and a small channel opens between the two shortly before they merge. Such an acceleration of the front velocity in the direction perpendicular to the cylinder axis had already been noticed in earlier investigations of the NO + CO reaction. There, this effect could be shown to be due to polishing scratches on the cylinder surface which strongly enhance the front velocity. In the present investigations no such macroscopic defects are identifiable in PEEM. It appears, however, to be reasonable to assume that here similar structural defects, albeit with a width below the resolution of our microscope, are present and cause the prenucleation. This hypothesis is further supported by the observation that prenucleation occurred only occasionally during the front propagation and then was strongly localized, indicating some peculiarity of these specific surface areas. Furthermore, the prenucleating islands are not as strongly distorted as the usual primary reaction fronts, suggesting some structural irregularities acting contrary to the omnipresent influence of surface steps aligned in the [001] direction.

A plausible picture of the prenucleation may be as follows. If some tiny scratches with diameters below the resolution limit of our microscope (~1 μm) come into contact with the advancing reaction front, the reaction may propagate quite rapidly along these channels until a highly reactive defect of larger size is reached. There, the reaction zone grows to a critical size and starts to expand in all directions, thus forming the reactive islands seen in PEEM. This explanation is consistent with earlier results which have shown that the propagation velocity of fronts in the NO + CO reaction is strongly enhanced by structural defects.

From the above presented explanation, we can further conclude that if defects whose sizes are well below the resolution of our microscope are able to propagate the reaction, such submicrometer defects could also be the cause for the seemingly "homogeneously" nucleated islands. Since the cylinder surface displays quite a number of inhomogeneities even on a scale as large as several micrometers, and as the NO + CO reaction is known to be extremely sensitive to the presence of defects, we strongly favor the idea of having only heterogeneous nucleation in the temperature range below the "surface explosion".

There are two basic difficulties with this interpretation, namely the existence of a critical temperature T_{crit} for the cooling process below which the nucleation process changes qualitatively and the observation that the reaction fronts do not always emanate from the same spots as one would expect for heterogeneous nucleation processes. Yet, a drastic change in the nucleation behavior with the cooling temperature can be made plausible if one assumes that two kinds of defects exist: a large number of small ones in the submicrometer range, the reactivity of which can be extinguished by cooling the sample below T_{crit}, and a few larger ones (several micrometers in size) which remain active even below this temperature.

The second difficulty, the variability in the nucleation sites, can be explained by two mechanisms: On the one hand, such a behavior can be expected if large fluctuations are present, and keeping in mind that we are always very close to the threshold where small defects become inactive, this possibility seems to be quite realistic. On the other hand, the chemical wave patterns which are present at higher temperatures might not have been completely removed during the cooling process, even though PEEM seems to demonstrate a completely unreactive surface. Thus, spatial inhomogeneities would be present in the system, which would affect the formation of nuclei in a seemingly random way, similar to fluctuations.

Unfortunately, we do not have enough information on the specific nature of the defects and their size distribution in order to come to a detailed picture of the role of defects in the nucleation of reaction fronts. While for the CO + O_2 reaction on Pt single crystals the critical size for front nucleation has been estimated to be about 1 μm, this size might vary considerably, depending on various factors like structural inhomogeneities and anisotropy in surface diffusion. As suggested by our experiments, the critical size of a defect can be well below this value, particularly for a surface reaction as sensitive to defects as the NO + CO reaction.

Although the topic of multistability and kinetic phase transitions in surface reactions has attracted a large amount of attention recently, the influence of defects has not yet been studied in great detail despite the important implications for surface reactions. In one Monte Carlo type study of an oscillatory, unimolecular decomposition reaction, Vlachos et al. conducted a systematic investigation of the influence of surface defects. Their simulations not only show the expected narrowing of the hysteresis loop with increasing amounts of defects on the surface but also demonstrate that a higher dispersion of a constant amount of defects has an even stronger narrowing effect on the hysteresis. This latter effect agrees nicely with our interpretation of nucleation...
Homogeneous and Heterogeneous Front Nucleation

at small (i.e. highly dispersed) defects in the experiments in which the sample was not cooled below $T_{\text{d}}$.

Compared to what is known for surface reactions, in which spatial inhomogeneities and nucleation clearly play a dominant role, very few experimental facts are known for fluid phase chemical reaction systems. In a study of a bistable fluid phase reaction, Roux et al. found a dependence of the transition points between the two branches of the bistable region on the stirring rate. This dependence has been interpreted by the authors as evidence for a nucleation-induced transition. However, this interpretation was questioned by Dewel et al. on the basis of mathematical simulations that demonstrated that the observed behavior most likely arises due to inhomogeneities in the reactor feeding rather than to fluctuations caused by thermal noise.

While the influence of insufficient mixing can be ruled out in our experiments due to the large mean free path of the gases under UHV conditions, it is still an open question whether thermal noise plays an important role in the present experiments. However, our experiments clearly show well-defined nucleation processes, although the detailed explanation still leaves room for further interpretation.

Summary

We have shown that the width of the bistable region below the so-called "surface explosion" in the platinum catalyzed reduction of NO by CO on Pt(100) and its vicinal orientations is strongly reduced by the presence of defects. While on an ideal, defect-free surface the hysteresis would extend over some 20 K, heterogeneous nucleation of reaction fronts at some large defects triggers an early transition from the unreactive to the reactive branch and decreases the width of the hysteresis by $\approx 7$ K. In addition, we could demonstrate that both homogeneous and heterogeneous nucleation of reaction fronts takes place, depending on the degree of supersaturation of the system. Homogeneous nucleation shows up in the occurrence of a "surface explosion".

For heterogeneous nucleation, which takes place below the temperature of the "surface explosion", we can further differentiate between two types of nucleation processes which we tentatively assign to two types of defects. While the activity of the smaller ones, whose size has to be in the submicrometer range, can be suppressed by cooling the sample sufficiently, the large defects (several micrometers in size) maintain their ability to act as nucleation centers independently of the starting temperature.

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References and Notes

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