

Parallel pathways in methanol decomposition on Pt(111)

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Abstract

The decomposition of methanol on the Pt(111) surface has been studied as a function of the incidence kinetic energy and the surface temperature using molecular beam techniques. Two parallel mechanisms are found. At low incidence energies and low surface temperatures methanol dissociates through a non-activated channel mediated by a molecular precursor. At high incidence energies direct dissociation over a barrier of ~ 0.5 eV occurs. The precursor channel is very sensitive to surface treatment while the direct channel is quite independent of this treatment. This indicates that the precursor channel occurs at minority defect sites, while the direct channel occurs on the majority terrace sites. The competition between these two channels in the reverse direction, recombinative methanol synthesis is also discussed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Surface dynamics studies on well defined metal single crystals have identified two fundamental classes of bond-breaking reactions at surfaces: direct dissociation of the molecule upon impact, and indirect dissociation via an adsorbed “precursor” state. These are typically characterized by different dependencies on the translational energy of the molecules and the surface temperature. In this paper we present the results of a system where both dissociation mechanisms occur in parallel. We show that a non-activated indirect channel can exist alongside a direct channel with a large activation barrier (~ 0.5 eV). This occurs through a

surface site dependence and modification of the surface allows us to control one of the channels. The non-activated, precursor mediated channel occurs at minority defect sites, while the activated, direct channel occurs at the majority terrace sites. Finally, from the dissociation dynamics, it is possible to make estimates for the recombinative desorption rate, the final step in the catalytic synthesis of CH_3OH . The importance of surface defects in determining the branching ratio between thermal and hyperthermal products of this reaction is discussed and may throw light on the interpretation of other dissociation/recombination systems where different mechanisms also may compete, such as hydrogen on silver [1].

The dissociation of methanol on a Pt(111) surface was chosen as it represents an ideal model for the reaction of small organic molecules at surfaces. Due to its industrial importance, the synthesis and reaction of methanol have been studied on a range

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of transition metal surfaces. On Pt(111), methanol is adsorbed intact at 100 K and it is generally believed that it decomposes to $H_{(ads)}$ and $CO_{(ads)}$ above 140 K [2,3]. In common with other methanol decomposition systems, discussed by Davis and Barteu [4], it is believed that the initial step in this reaction is the cleavage of the O–H bond to produce surface methoxy and hydrogen. While methoxy is stable on other metal surfaces, on Pt(111) it undergoes rapid and complete decomposition [2]. This means that the rate limiting step of the complete reaction, i.e. producing gas phase CO and H_2 , is the dissociative chemisorption of CH_3OH , breaking the O–H bond and forming adsorbed methoxy and hydrogen (see Figs. 1 and 5). Since this is the interaction of a gas phase species with a surface, it is open to direct study with supersonic molecular beam techniques. We do note that other authors claim that CH_3OH partially decomposes by C–O bond scission on Pt(111) and other metals [5], although the observation of this channel is apparently very dependent upon details of the surface structure. We find no evidence for any C–O bond scission on our sample, as discussed later.

2. Experimental

The experiments were performed in a UHV system previously described in detail [6]. It consists of a main chamber with a base pressure of 1×10^{-10} Torr, to which is attached a three stage

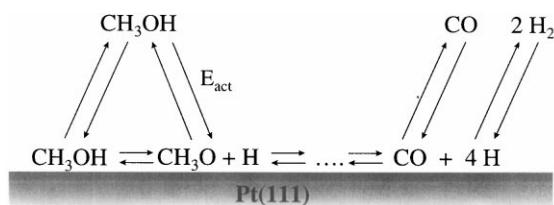


Fig. 1. Schematic description of the methanol decomposition (synthesis) over a transition metal surface. The first step is the breaking of the O–H bond, either via an adsorbed methanol precursor state, or directly over an activation barrier. The methoxy species then rapidly decomposes to $CO_{(ads)}$ and $H_{(ads)}$, which then desorb at sufficiently high surface temperatures.

supersonic molecular beam source. A seeded methanol beam was formed by bubbling a high purity carrier gas (He, H_2 , Ar or N_2) through a flask of spectroscopic grade methanol. The kinetic energy of the methanol molecules could be varied between 0.10 and 1.02 eV by changing the carrier gas and nozzle temperature, and was measured by their time-of-flight from a mechanical chopper to a quadrupole mass spectrometer (QMS) in the scattering chamber. The beam was always at normal incidence to the surface.

The Pt(111) crystal had been characterized in a number of previous studies [6] and was cleaned by cycles of Ar^+ ion bombardment, oxidation (1×10^{-7} Torr, 700 K) and vacuum annealing (1150 K). The crystal was heated by electron bombardment of the backside. The cleanliness was checked by Auger electron spectroscopy (AES) and the defect density was monitored by the well characterized CO temperature programmed desorption (TPD) peak shape [7,8] and by specular helium scattering, which is an extremely sensitive probe of surface defects.

Sexton investigated the interaction of methanol with Pt(111) using electron energy loss spectroscopy (EELS) and TPD. He found that the decomposition of methanol on Pt(111) yields only $CO_{(ads)}$ and $H_{(ads)}$. A TPD of a methanol covered surface resulted in the desorption of only methanol, H_2 and CO. No dehydrogenated intermediate species such as methoxy have ever been observed on this surface with EELS, indicating the rapid and exclusive generation of stoichiometric amounts of CO and H_2 [2]. This was further verified in our studies by looking for other desorbing reaction products such as water, CO_2 and CH_4 during molecular beam dosing. No such species were ever detected. Such species, if present, were at least 100 times smaller than the dominant CO and H_2 desorption products and indicate that C–O bond scission was not a significant decomposition channel on our sample.

The rate of decomposition can thus be measured either by following the removal of methanol from the beam by the King and Wells method [9], or the production of H_2 or CO which desorb from the surface at 360 and 470 K, respectively. The

CO and H₂ productions were linearly proportional to each other, but in practice we found that we were more sensitive to the production of H₂. By measuring the H₂ signal with a non-line-of-sight QMS and normalizing to the incident flux of methanol, we were able to obtain a relative decomposition probability. Due to the uncalibrated sensitivity of the QMS to methanol and hydrogen this data is in arbitrary units. The absolute reaction probability of methanol was also measured by the method of King and Wells [9]. Under the conditions of maximum decomposition shown in Fig. 2,

we were just able to resolve the uptake of methanol by the reaction, placing the maximum probability at approximately 1%. We have scaled the arbitrary units of the relative signal to this value, so that to a first approximation the relative scale can be read as a percentage dissociation probability per collision.

In measurements taken below 500 K some poisoning of the reaction was observed as a function of time due to the slow build up of CO_(ads). All the data presented here were taken in the zero coverage limit where this poisoning was insignificant.

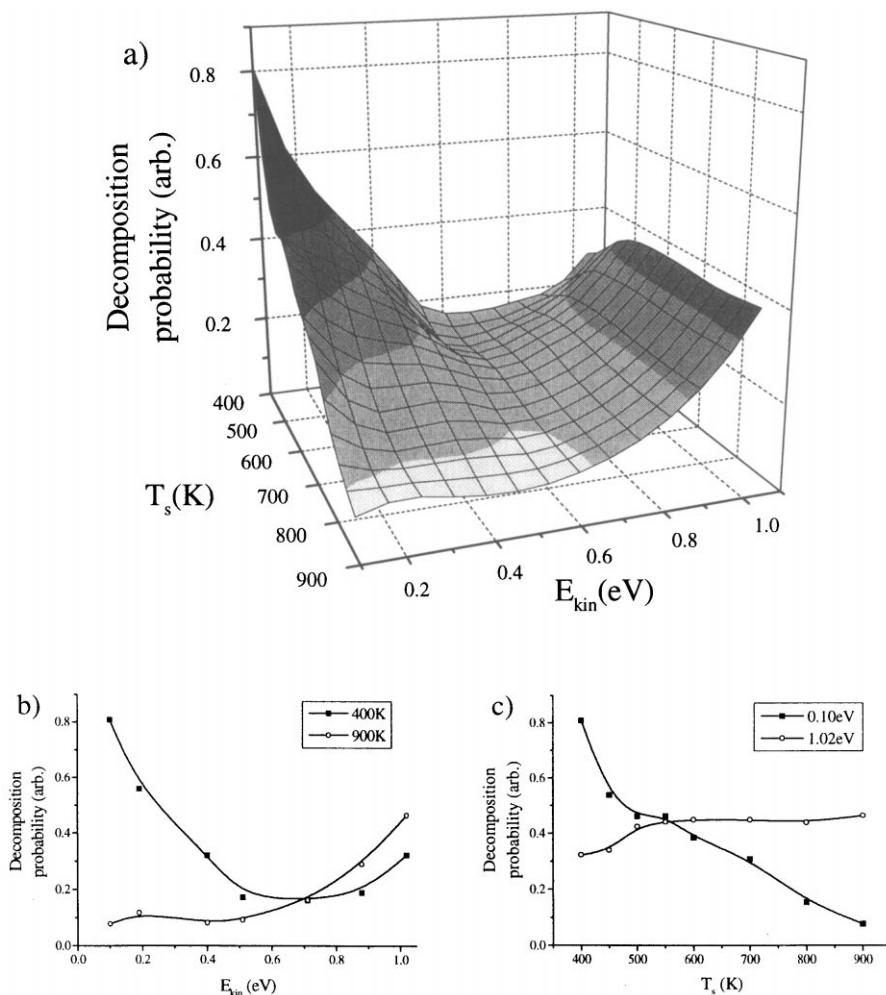


Fig. 2. (a) Relative methanol decomposition probability [arbitrary units \approx dissociation probability per collision (%)] as a function of surface temperature (T_s) and incidence beam energy (E_{kin}). (b) Same data as a function of incidence energy, $T_s = 400$ and 900 K. (c) Same data as a function of surface temperature, $E_{kin} = 0.10$ and 1.02 eV.

3. Results and discussion

3.1. The decomposition mechanism

The relative decomposition probability was measured at surface temperatures between 400 and 1000 K and with incidence beam energies between 0.10 and 1.02 eV. The results are shown as a 3D plot in Fig. 2a and as cuts through this plot in Fig. 2b,c. There are two distinct regions of high decomposition probability. At incidence beam energies below 0.5 eV the probability rises sharply with decreasing beam energy and surface temperature. At incidence beam energies above 0.5 eV the decomposition probability rises with increasing beam energy, and is almost independent of the surface temperature. These two types of behavior are typical of dissociation mechanisms characterized in studies of many other molecules at surfaces.

The dependence on both incident energy and surface temperature for the low incidence energy pathway is exactly the behavior anticipated for a molecular precursor. The mechanism in this regime is thus assigned to an indirect mechanism, mediated by an adsorbed molecular methanol precursor. Under these conditions the rate of dissociation is limited by the population of the methanol precursor. Decreasing the kinetic energy of the molecules increases the probability of trapping into this weakly bound state, and decreasing the surface temperature increases the ratio of dissociation over the more activated desorption of the adsorbed methanol precursor. Thermal desorption studies [2] indicate that the molecular methanol well depth on Pt(111) is approximately 0.5 eV. This is consistent with a high probability of trapping into this well over the approximate incidence energy range 0–0.5 eV, as is well known from soft cube models of sticking (see for example Ref. [10]).

The high incidence energy regime behaves as a direct dissociation mechanism involving a considerable energetic barrier. The threshold for dissociation via this mechanism is seen at approximately 0.5 eV in Fig. 2. Since thresholds in molecular beam translational excitation experiments are roughly equivalent to thermal activation barriers, we infer that the thermal barrier is roughly of this

magnitude. Clearly the dissociation increases slowly with incidence energy above this threshold, indicative of a distribution of barriers characteristic of any multidimensional dynamic process. No such direct channel was observed by Gibson and Dubois in earlier beam studies [3]. However, they were limited to kinetic energies below 0.25 eV and in this energy regime their conclusion that dissociation is dominated by an indirect mechanism is fully in agreement with our observations.

Since molecules dissociating directly upon collision with the surface do not equilibrate to the surface temperature this channel might be expected to be surface temperature independent. While this is generally true above 500 K, a small dependence is observed in the form of a “step” below 500 K. A possible explanation for this lies in the kinetics of the subsequent decomposition on the surface.

Looking for an isotope effect confirmed that the rate limiting step is the breaking of the O–H bond. The decomposition probability for deuterated methanol, CH₃OD, was determined by measuring the rate of CO desorption. We found that dissociation through the direct channel, $E_{\text{kin}}=0.81$ eV and $T_s=1000$ K, was decreased by approximately 20%, and by 12% through the indirect channel, $E_{\text{kin}}=0.075$ eV and $T_s=550$ K.

3.2. Role of surface treatment

We would like to explain the simultaneous presence of a non-activated, precursor mediated dissociation channel on a surface that also presents a high barrier to the direct dissociation of molecules approaching from the gas phase. Common arguments for such a coexistence invoke a highly restricted phase space at the low energy barrier, but it is difficult to reconcile the simultaneous existence of both a low and high barrier at the same site on the surface.

We have found that we were able to modify the activity of the surface to methanol dissociation substantially for the precursor channel by exposing the surface to O₂ followed by a flash to high temperatures. A surface treatment similar to this was commonly employed by us to ensure that all surface carbon contaminant was removed. This treatment consists of exposure to ca. 50 L of

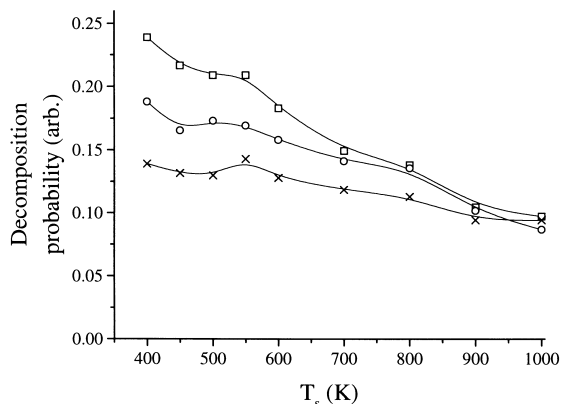


Fig. 3. Methanol decomposition probability as a function of the surface temperature on a clean surface (squares) and following one (circles) and two (crosses) oxidation/flash treatments. $E_{\text{kin}} = 0.45$ eV.

oxygen at room temperature followed by five brief flashes to 1150 K in UHV. Fig. 3 shows a series of measurements made on a clean surface, and the same surface following oxygen/flash treatments. Such a treatment significantly reduces the methanol decomposition probability at low surface temperatures, where the precursor channel is dominant, while at high surface temperatures, where the direct channel is dominant, the decomposition is unaffected. This is confirmed in Fig. 4, where the same experiment has been performed as a function of the incidence methanol energy at

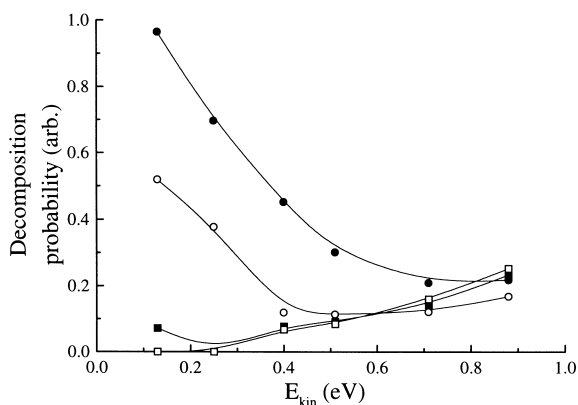


Fig. 4. Methanol decomposition probability as a function of incidence energy on a clean surface (solid points) and following one oxidation/flash treatment (open points). $T_s = 400$ K (circles) and 1000 K (squares).

two surface temperatures. At low energies and low surface temperatures the indirect channel is strongly suppressed by the oxygen treatment, while at high surface temperatures, where the direct pathway is dominant, the decomposition probability is unaffected. A second such oxygen/flash treatment quenches the precursor channel even more, but additional oxygen/flash treatments have no further effect on activity. After the oxygen/flash cycles have quenched the activity of the precursor channel, extended periods of annealing (20 min at 1150 K) did restore the original activity of the surface to the precursor channel.

Oxygen desorbs from Pt(111) at a temperature of 750 K [6,11], and should be completely removed in a single flash to 1150 K. This was confirmed to levels below 1% by the absence of an oxygen AES peak. Such oxygen/flash cycles are generally accepted procedures for cleaning residual carbon from the Pt(111) surface, and have been proven quite effective for this purpose on our sample as well. No changes (other than the removal of residual surface carbon) were detectable by Auger spectroscopy in the chemical structure of the surface by the oxygen/flash treatment. For most species, the sensitivity limits mean that all such chemical changes are typically less than 1% of a monolayer. In addition, there was no change in the CO thermal desorption peak shape. This TPD peak shape shows a small shoulder to the high temperature side characteristic of ca. 2.5% defects (believed to be steps due to a slight miscut of the crystal). This also suggests that there was no detectable change in the overall defect density due to the oxygen/flash cycles. In order to further characterize whether such an oxidation/flash procedure had any measurable changes in the defect density, specular He atom scattering was employed since the intensity of this is well known to be extremely sensitive to defects/residual impurities. No changes were observed following the oxidation/flash treatment in the specular scattering of a 63 meV supersonic nozzle He atom beam detected with a rotatable detector with 1.5° angular aperture. Again, this infers that there was no substantial change in the dominant defect density (presumably steps) nor in their spatial distribution following the oxidation/flash.

Even though the oxygen/flash treatment had a strong effect on the precursor channel, we were unable to detect any differences of the surface. This leads us to conclude that the density of sites affected by the oxygen/flash treatment, and responsible for the indirect dissociation, is an extremely small minority site on the surface, certainly less than 1% of all sites. Certainly, the most obvious candidate for such a reactive, low density site is some type of surface defect, consistent with the findings of ref. [3]. This leads us to speculate that oxygen may selectively block these sites, as suggested below, without any measurable effect on the direct dissociation channel. It is likely that the flat (111) terraces remain unaffected by the oxygen/anneal treatment, and it is thus suggested that the direct dissociation occurs on the (111) terraces.

We can only speculate as to the identity of the minority defect site responsible for the precursor channel since it is not directly observed. It is unlikely to be the dominant defect sites, e.g. steps, since there were no observable changes via oxidation/flash in the CO TPD or specular He scattering. Other possibilities are kink sites, minority chemical defects, etc. We note, however, that while a single flash to 1150 K was insufficient to regenerate the activity of the indirect channel, extended periods of annealing did restore the surface to its original activity. The poisoning of the surface activity by oxidation and slow regeneration of this activity is quite reminiscent of the formation and decomposition of silicon oxides on the Pt(111) surfaces. While silicon is thermodynamically unstable at the surface under vacuum, in the presence of surface oxygen it is suggested to form stable Pt–Si–O oxides [12]. These were seen to form rapidly and slowly decompose above 1100 K in vacuum [13]. Although we were unable to observe these oxides by Auger electron spectroscopy, this simply implies that any such oxides were present at coverages below 1% of a monolayer, and confirm the low Si bulk content of our crystal. One possible scenario for the poisoning of the precursor dissociation via oxidation and subsequent reactivation by extended anneal is that the oxidation causes Pt–Si–O oxides to form or diffuse to these specific active defect sites, thereby decorating them,

while the extended anneal dissociates these oxides and reforms the active defect site.

We also consider the contrary hypothesis, i.e. that the extended annealing causes bulk defects/impurities to diffuse to the surface, while the oxygen/flash treatment removes these defects/impurities. However, within the limits of Auger sensitivity, the extended anneal caused no chemical impurities to build up on the surface. Nor did the CO TPD or specular He scattering show any increase in defect concentration with the extended anneal. We therefore consider this possibility less likely.

3.3. Surface kinetics

It is impossible from this study to model fully the decomposition kinetics on the surface following the initial O–H bond dissociation. However, the parameters obtained for the dissociation step can be used to provide information on the kinetics of the reverse process, methoxy plus hydrogen recombinative desorption, the final step in the methanol synthesis reaction (on single crystal surfaces).

By microscopic reversibility, the same direct and precursor mediated channels can operate for desorption as in adsorption (Fig. 5). Under conditions of thermal equilibrium, the branching ratio of recombination through the direct and indirect channels is then given by Eq. (1). If we assume that the rate limiting step for desorption through the indirect channel is the recombination of methoxy and hydrogen on the surface, Eq. (1) will

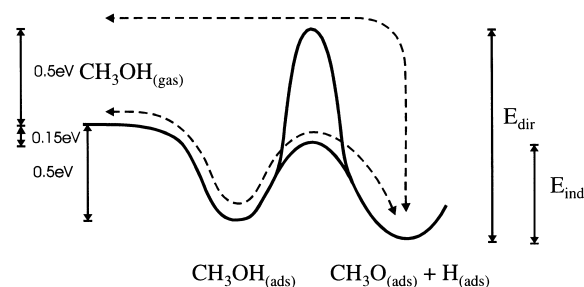


Fig. 5. Schematic potential energy diagram for methanol dissociation (recombinative desorption) on Pt(111). Energy levels are based on results presented here and estimates taken from previous studies.

also express the branching ratio of desorption through the two channels:

$$R_{\text{dir/ind}} = \frac{v_{\text{dir}} \exp(-E_{\text{dir}}/k_{\text{B}} T_{\text{s}})}{v_{\text{ind}} \exp(-E_{\text{ind}}/k_{\text{B}} T_{\text{s}})}, \quad (1)$$

where E and v are the activation barriers and the prefactors for recombination through the direct (dir) and indirect (ind) channels (see Fig. 5). If we take the simplest approximation, that the prefactor through the indirect channel is the same as the direct channel modified by the relative defect density, $v_{\text{ind}} = v_{\text{dir}} \rho_{\text{def}}$, then this simplifies to Eq. (2):

$$R_{\text{dir/ind}} = \frac{\exp[-(E_{\text{dir}} - E_{\text{ind}})/k_{\text{B}} T_{\text{s}}]}{\rho_{\text{def}}}. \quad (2)$$

Assuming detailed balance, i.e. that the desorption experiment averages over the same phase space as the molecular beam sticking experiment, then the difference in barriers is obtained directly from our molecular beam studies. While this assumption is in no way guaranteed, there are only a few documented exceptions where detailed balance is not a “good” approximation [14]. The threshold to the direct channel shows that E_{dir} lies ~ 0.5 eV above the zero point energy of the gas phase molecule. A fit of standard precursor kinetics to the temperature dependence of the low energy, indirect channel data shows that E_{ind} lies 0.15 eV below the zero point energy of the gas phase molecule, hence $E_{\text{dir}} - E_{\text{ind}} = 0.65$ eV (Fig. 5). $R_{\text{dir/ind}}$ then varies from 1×10^{-9} on a cool surface (300 K) with a relatively high defect concentration (1%), to 0.8 on a surface with very few defects (0.01%) at 800 K. Indeed, under most conditions $R_{\text{dir/ind}}$ will be significantly less than 1, indicating that the precursor mediated channel will dominate the desorption process. Thus, the low energy pathway not surprisingly is anticipated to dominate desorption kinetics for most realistic surfaces.

The authors note that several small temperature dependent features are seen in the results, for instance at 550 K in Fig. 3. While the relative strength of these features varied somewhat depending on exact surface treatment, they were always present as shown in Fig. 3, and were very reproducible for a given surface treatment. Although these features were principally observed for the precursor mediated dissociation channels, we suspect

they reflect some competition in the subsequent decomposition kinetics.

Finally, it is possible that other systems reported to show an apparent contradiction between adsorption and desorption mechanisms also involve the type of site dependence observed here for methanol on Pt(111). For example in the case of D_2 on silver [1] the very weak binding of the molecule to the surface makes trapping into a precursor state unlikely at the incidence energies available in most molecular beam studies. Instead, direct dissociation pathways with large activation barriers dominate the adsorption dynamics. However, in desorption studies molecules have been observed to leave the surface at low energies, close to thermal equilibrium with T_{s} . The branching ratio in adsorption is limited by the instability of the molecular hydrogen precursor and in desorption by the defect density. On Ag(111) the ratio between high and low energy D_2 desorbing from these channels is indeed seen to be strongly surface temperature dependent [1], consistent with Eq. (2).

4. Conclusion

This molecular beam study of methanol decomposition on Pt(111) has shown two different pathways to dissociation of the molecule on the surface. A non-activated channel that goes via a molecular precursor and an activated channel, where the molecule dissociates directly upon impact over a barrier of ~ 0.5 eV. We found that the precursor channel was strongly affected by the preparation of the surface, where oxygen/flash treatments decreased the decomposition probability. We suggest that the effect of the oxygen/flash treatment is due to the formation of a Pt–Si–O compound at minority defect sites where the precursor channel occurs, and thereby hinders the decomposition. The direct channel was unaffected by this, and is therefore suggested to occur on the (111) terraces.

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