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A structural effect in direct reactions: kinetics of D abstraction from Pt(110) 1 × 2 surfaces with gaseous H atoms

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Abstract

Deuterium-covered Pt(110) surfaces were subjected to a flux of thermal H atoms at 100 K. The rates of product formation, HD and D_2, were measured simultaneously with H atom exposure as a function of D coverage. D_2 as a product and the kinetics of HD formation contradict the operation of Eley–Rideal type mechanisms in these reactions. More appropriate seems the assumption that a hot-atom type mechanism operates in abstraction of adsorbed D by gaseous H. The H/D abstraction kinetics at Pt(110) surfaces are completely different from that observed previously at Pt(111) surfaces. This structural effect puts a further question mark on the validity of the Eley–Rideal mechanisms in abstraction reactions and is interpreted in the present work as a consequence of the interrelation between a hot-atom mechanism and the surface structure of the reconstructed substrate. © 1998 Elsevier Science B.V.

1. Introduction

Reactions of adsorbates with gaseous H atoms have attracted a growing interest recently. In particular, the simplest feasible reaction, abstraction of D adsorbed on metal surfaces by H towards a gaseous HD product molecule was studied for various systems, Cu(111) [1,2], Ni(110) [3], Ni(100) [4], Al(100) [5] and Pt(111) [6]. As the incoming atom is not accommodated at the surface prior to reaction, the HD product molecule is expected to carry significant energy. This was confirmed in laser spectroscopy–molecular beam studies by Rettner and coworkers [1,2] on abstraction from Cu(111) surfaces. They observed that the reaction energy of ~2.5 eV is distributed in translational, rotational and vibrational degrees of freedom of the product.

The kinetics of abstraction of D by H expressed as an Eley–Rideal (ER) process via

$$\mathrm{d(HD)}/\mathrm{d}t = (\mathrm{D})\,\sigma\Phi \tag{1}$$

reveals as the rate of formation of the product

$$\mathrm{d(HD)}/\mathrm{d}t = (\mathrm{D})_0\,\sigma\Phi\exp(-\sigma\Phi t)\,, \tag{2}$$

where σ is the reaction cross-section, Φ is the H atom flux and $(\mathrm{D})_0$ is the D coverage at the start of the reaction. To obtain the solution (2) it is necessary to assume that the atom flux is directed at the surface as a step function located at $t = 0$. It is clear from the rate expression (2) that the rate assumes its maximum at $t = 0$ and decreases exponentially thereafter.

Kinetic studies performed in this laboratory on the abstraction of D from Ni(100) [4] and Pt(111) [6] surfaces revealed that the time (fluence) dependen-

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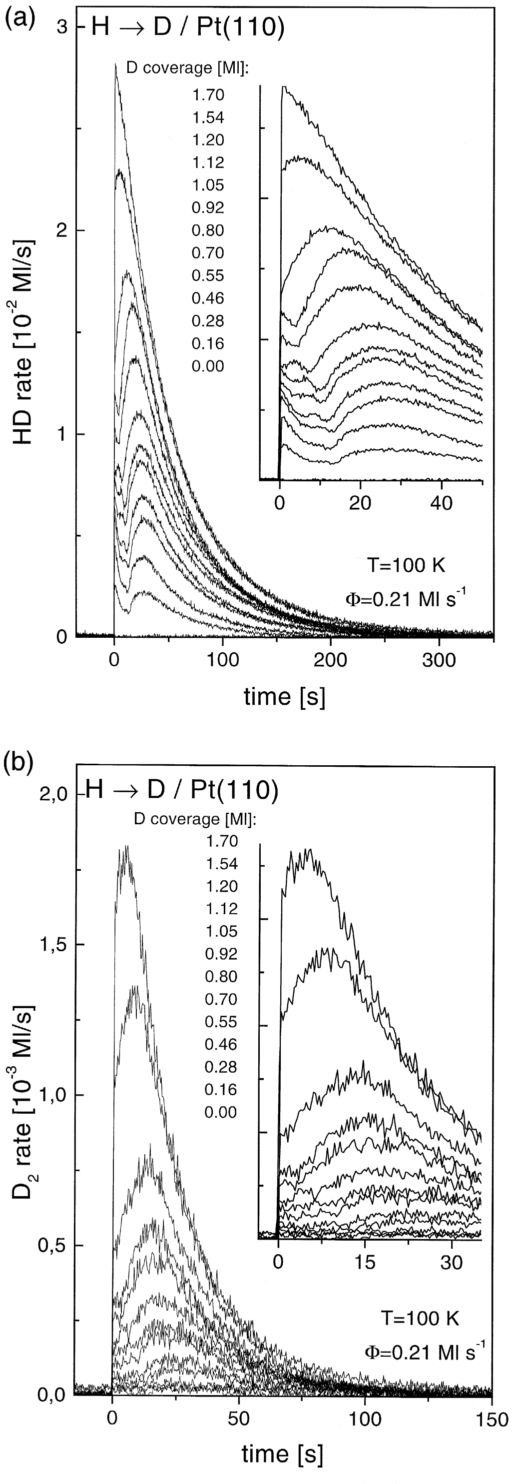

Fig. 1. HD (a) and D_2 (b) reaction rates measured upon subjecting D-covered Pt(110) surfaces to a flux of H atoms. H atom flux 0.21 Ml s^{-1}, substrate temperature 100 K. The D coverages given in the figure are those at reaction start (time = 0).

cies of experimental HD rates differ substantially from the predicted ones. At the reaction start (H flux on) the rates jump to specific coverage-dependent values R_0, but increase later on. After reaching maximum values at $t = t_m$, the rates drop exponentially controlled by cross-sections, which are of the order of Å^2. The magnitude of R_0 does not increase linearly with the D coverage. The lengths of the induction periods t_m, decrease with increasing D coverage. If H is coadsorbed at saturation, t_m is independent of coverage and the initial rates R_0 scale linearly with the partial D coverage.

In addition to HD, homonuclear reaction product molecules D_2 were observed in both studies, as were reported earlier in abstraction experiments at Ni(110) surfaces [3].

According to these experimental findings, ER mechanisms do not provide a correct description of the abstraction kinetics for these reactions. As an alternative description of direct reactions, the hot-atom [7] reaction pathway has been suggested. Reaction trajectories calculated in recent molecular dynamics simulations of abstraction of H by H from Si(110) [8,9] and Cu(111) [10–14] surfaces confirm the existence of hot-atom reactive trajectories and homonuclear reaction products. These theoretical studies also reveal that the products carry the reaction energy in internal excitations [8–14].

The present investigation was performed in order to explore whether a structural effect exists in abstraction. As within the Eley–Rideal picture the surface geometry is irrelevant for the rate of a product, a structural effect in the rates would raise further questions on the validity of this mechanism for atom/adsorbate reactions.

2. Experimental

The experiments were carried out in the UHV system used in the previous study on Ni(100) surfaces [4]. In this system, the H atom source and the mass spectrometer for monitoring the reaction product are contained in a separately pumped UHV system (source chamber) attached to a main chamber which houses the sample and surface analytical tools. During the reaction, the sample is placed in front of an aperture which connects the main and source chamber. This aperture can be closed by a shutter and at the opening of the shutter the sample surface is exposed to a flux of H atoms from the atom source. The atom source consists of a heated W tube according to the design by Bischler and Bertel [15]; however, the electron beam heating of the tube was replaced by ohmic heating. The atom flux from the source was determined from the tube front end temperature (2000 K) and the hydrogen gas throughput through the tube. The flux in monolayer/s is expressed with respect to the areal atom density on the unreconstructed Pt(110) surface, 1 Ml $s^{-1} = 0.92 \times 10^{15}$ cm^{-2} s^{-1}.

After proper cleaning, hydrogen desorption spectra were found in excellent agreement with the spectra published by Anger et al. [16]. These authors reported 1.7 Ml as the H saturation coverage, which was confirmed from the present spectra within an error margin of 10%.

3. Results and discussion

HD and D_2 were recorded as the reaction products. The fluence dependence of the rates of these products are shown in Fig. 1a and Fig. 1b as a function of D coverage prior to reaction at a constant H flux of 0.21 Ml s^{-1} and 100 K sample temperature. After reaction completion, thermal desorption spectra confirmed that no D was left at the surface, indicating complete abstraction. As all preadsorbed D have to appear in HD or D_2 products, the D saturation coverage could be used to convert the HD and D_2 signals measured by the quadrupole into units of Ml s^{-1}, as was done in Fig. 1.

Up to a D coverage of ~ 1 Ml the HD rate curves in Fig. 1a exhibit a common behavior. At the opening of the shutter they jump to a finite value, decrease and increase again. After having reached an absolute or relative maximum at the end of an induction period, the rates decay exponentially, confirmed by a logarithmic plot of the HD rate curves. At D coverages of 1.2 and 1.55 Ml the rates increase immediately after the rate jump and at a coverage of 1.7 Ml the rate decreases right after the jump. Evaluation of the late rate fluence dependence of all rate curves shown (beyond the induction period) in terms of an exponential law as expressed in Eq. (2) reveals

~ 1 Å^2 as the reaction cross-section, irrespective of D coverage.

The rate curves at small D coverages in Fig. 1a exhibit in the induction period, corresponding to the first few Ml of atom fluence, a fine structure which was reproduced several times. These structures are not artifacts. As seen in Fig. 1a, the induction period is longer at smaller D coverages.

The D_2 rates measured (almost) simultaneously with the HD rates shown in Fig. 1b exhibit similar behavior to the HD rates: a rate jump at the start of the reaction, a rate increase in the induction period, followed by a rate decay. The D_2 rate induction period has the same length as the respective HD rate induction period. The late rate decay is twice as fast as the HD rate decay, which can be verified by a logarithmic plot (no perfect line as opposed to the HD rate plot). A 'reaction cross-section' towards D_2 of twice the HD formation cross-section was obtained. The quotation marks are used in order to emphasize that the cross-section towards D_2 is only indicative for the efficiency of the process and not a real cross-section as D_2 formation is a second-order process.

The bottom curve in Fig. 1a was measured without preadsorbed D in order to confirm that background effects were negligible. Likewise, control experiments with a cold tube revealed no products at all, indicating that H adsorption via D displacement can be neglected at 100 K. At higher temperatures $T > 150$ K, this is not the case, as expected.

The yields towards HD and D_2 and corresponding rate steps deduced from Fig. 1 are shown in Fig. 2. The D_2 yields can be fitted excellently with a square dependence on the D coverage, in accordance with a second-order process. This phenomenon was also observed for the D_2 rates in the previous studies on the abstraction kinetics on Ni(100) [4] and Pt(111) [6]. The HD yields seem to be approximated well by a linear dependence, of the D coverage, which is, however, misleading. The HD yields have to exceed the magnitudes deduced from a linear coverage dependence as the yield of the competing D_2 product scales with the square of the D coverage. As at most 11% of the adsorbed D appear in the D_2 reaction channel, the deviation of the HD yield from a linear relationship is not very significant but the data shown in Fig. 2 are in line with this. A similar conclusion can be drawn from the HD yields measured earlier at Ni(100) and Pt(111) surfaces.

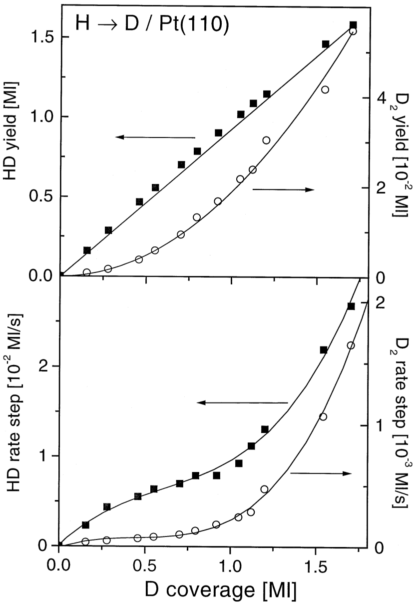

Fig. 2. HD and D_2 yields and HD and D_2 rate steps at reaction start deduced from Fig. 1.

The rate jumps shown in Fig. 2 do not exhibit a simple functional dependence. Neither is the HD rate jump linear in the D coverage nor does the D_2 rate jump depend on the square of the D coverage.

Leaving aside the formation of D_2, the kinetics of HD formation does not exhibit the expectations drawn from the operation of an ER reaction mechanism, as was already concluded from the kinetics measured previously in the abstraction reactions on Ni(100) and Pt(111) surfaces. Only in the late reaction regimes are exponential decays according to Eq. (2) observed on Ni(100), Pt(111) and the present Pt(110) surface. The results reported for abstraction from Ni(110) [3] and Al(111) [5] surfaces do not provide detailed information on the initial reaction period and data on coverage dependence, both of which are critical for an analysis of the reaction mechanism.

The kinetics of HD and D_2 formation in the induction period measured in the present study at Pt(110) surfaces is completely different from that measured earlier at Pt(111) surfaces. At Pt(111) surfaces the HD and D_2 rates jump at the opening of the shutter to significantly smaller values than reported here and they stay small throughout the induction period. Only late in the induction periods do the rates increase and assume their maximum values.

Accordingly, the abstraction kinetics is sensitive to the surface structure which contradicts the ER reaction scheme.

In the previous work on D abstraction by H from Ni(100) [4] and more explicitly in the Pt(111) paper [6], it was argued that a hot-atom mechanism is much more appropriate to explain the measured product kinetics, in particular the occurrence of a D_2 product and the observation that the HD product rates at the opening of the shutter are smaller than they could be at the given D coverage, i.e. the rates do not assume their maxima right at the beginning of the reaction.

A feasible hot-atom mechanism based scenario starts with the assumption that H atoms impinging from the gas phase stick at empty surface sites, produce hot H atoms upon encountering H-occupied sites and hot D or H atoms upon encountering D-occupied sites, each event with a given probability, pstick, pHHH, pHDH and pHDD. Hot H and D atoms generated in these collisions travel on the surface and pass along empty, H- and D-occupied sites. With probabilities photstick and photreact they stick at empty sites and react at occupied sites. If the probabilities pstick and photstick are assumed to be bigger than the reaction probability photreact, a competing step to reaction is introduced which, by construction, causes a coverage-dependent induction period by reducing the product rates as long as the surface exhibits empty sites. Only if the coverage has approached saturation by the sticking of incoming and hot atoms, do the product rates assume their maximum values and decrease exponentially at later times. Note that within this scenario the homonuclear D_2 reaction products are generated by the events controlled by the probability pHDD. The second-order kinetics for D_2 formation follows automatically, as well as the induction period in the D_2 reaction channel.

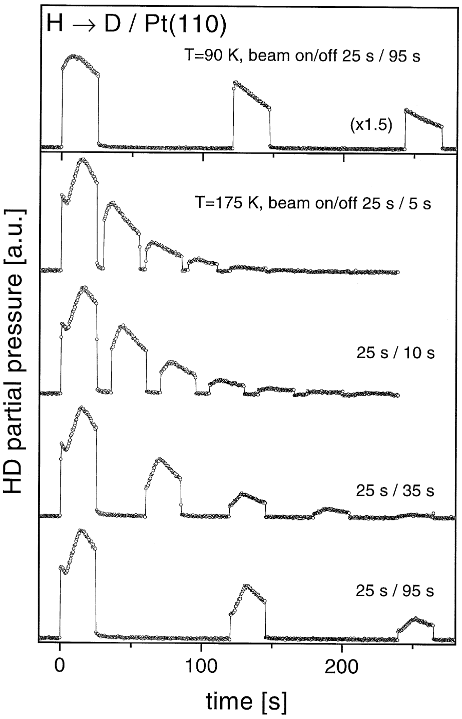

Fig. 3. Interrupted flux reaction HD rate measurements measured at D-covered Pt(110) surfaces at a H flux of 0.2 Ml s^{-1}. Top curve: substrate temperature 90 K, bottom curves: reaction temperature 175 K. The shutter open/closed periods are assigned to each rate curve.

The consequences of this scenario can be tested experimentally. If the beam of H atoms is interrupted in the late reaction period and switched on again at a later time, the rate jump should immediately be followed by a rate decay, rather than exhibit a new induction period as the coverage remained at its saturation value. The top rate curve in Fig. 3, measured at 90 K at a D coverage of 1.2, shows the outcome of such an experiment. In accordance with expectations from the above scheme, only after the first opening of the shutter is a rate increase/decay sequence observed. At later opening events the rate jumps to the value which was already reached at the time of the previous shutter closing event.

The experiment was repeated at 175 K with various shutter open/closed periods. At 175 K isothermal desorption from a hydrogen-saturated surface occurs. Therefore, after every ‘shutter closed’ period a new induction period with a rate increase following the rate jump should be observed. As seen in the bottom curves of Fig. 3 this is indeed the case. Moreover, with increasing shutter closed periods, 5–35 s, through isothermal desorption the hydrogen (D plus H) coverage decrease gets more pronounced and, accordingly, the length of the induction period increases. The rate curves in Fig. 3 suggest that after

35 s isothermal desorption has established an equilibrium coverage, as no changes in the induction periods and rates are observed at the even longer shutter closed period of 95 s.

From the above model construction it is immediately clear that reactions at surfaces, on which a fractional D coverage and H coadsorption at saturation were established, exhibit induction periods of length which do not depend of the D coverage, as was observed experimentally in the present and previous studies from this laboratory.

The general features of the rate curves in Fig. 1 for abstraction from Pt(110) surfaces, as well as the rates measured in the previous studies with Ni(100) [4] and Pt(111) [6] surfaces, are explained within the hot-atom scenario and can be rationalized by model calculations of the kinetics based on a random walk scheme [17] with the parameter settings pstick = 1, photstick = 1 and preact = 0.01–0.1. However, as the HD rates in Fig. 1a illustrate, in the initial reaction period at Pt(110), there is an almost ER-type behavior, which is absent at Pt(111) surfaces: a rate jump followed by a fast rate decrease. It seems as if on Pt(110) surfaces a small ER contribution without an induction period effect dominates initially at small coverages, at later times and higher coverages overruled by the hot-atom scenario. At Pt(111) this initial jump/decrease phase is absent, only a pronounced hot-atom induction period exists, more pronounced than at Ni(100) surfaces.

The structural difference between the Pt(111) and Pt(110) surfaces is the corrugation of these surfaces. The Pt(111) surface is flat and the Pt(110) surface is highly corrugated due to its 1×2 reconstruction with tilted (111) oriented plane segments. This corrugation introduces a directional anisotropy which can cause the movement of hot atoms across the surface to exhibit directional restrictions. It might be that they move predominantly along the channels provided by the reconstruction. Due to this effect, hot atoms on Pt(110) surfaces might have a limited chance to stick at empty sites, as only the sites in those channels are available for sticking, thereby reducing the induction period effect. This phenomenon could be even amplified by the structure of the adsorbed D layer to be abstracted. If D gets predominantly adsorbed in chains along the channels, the D reactants would be arranged and the H reactants move in a restricted geometry. As these restrictions are absent on Pt(111) surfaces the abstraction kinetics on that surface is expected to differ from the present Pt(110) surface.

4. Summary

In summary, we have shown that the kinetics of abstraction reactions exhibit surface structure sensitivity. This observation contradicts the operation of Eley–Rideal mechanisms in these reactions. Hot-atom type reaction scenarios seem to provide a much more appropriate description.

References

[1] C.T. Rettner, Phys. Rev. Lett. 69 (1992) 383.

[2] C.T. Rettner, D.J. Auerbach, J. Chem. Phys. 104 (1996) 2732.

[3] G. Eilmsteiner, W. Walkner, A. Winkler, Surf. Sci. 352/354 (1996) 263.

[4] Th. Kammler, J. Lee, J. Küppers, J. Chem. Phys. 106 (1997) 7362.

[5] J. Boh, G. Eilmsteiner, K.D. Rendulic, A. Winkler, Surf. Sci. 395 (1998) 98.

[6] S. Wehner, J. Küppers, J. Chem. Phys. (in press).

[7] J. Harris, B. Kasemo, Surf. Sci. 105 (1981) L281.

[8] P. Kratzer, J. Chem. Phys. 106 (1997) 6752.

[9] P. Kratzer, W. Brenig, Surf. Sci. 254 (1991) 275.

[10] B. Jackson, M. Persson, J. Chem. Phys. 96 (1992) 2378.

[11] M. Persson, B. Jackson, J. Chem. Phys. 102 (1995) 1078.

[12] M. Persson, B. Jackson, Chem. Phys. Lett. 237 (1995) 468.

[13] B. Jackson, M. Persson, J. Chem. Phys. 103 (1995) 6257.

[14] S. Caratzoulas, B. Jackson, M. Persson, J. Chem. Phys. 107 (1997) 6420.

[15] U. Bischler, E. Bertel, J. Vac. Sci. Technol. A5 (1993) 485.

[16] G. Anger, H.F. Berger, M. Luger, S. Feistritzer, A. Winkler, K.D. Rendulic, Surf. Sci. 219 (1989) L583.

[17] Th. Kammler, S. Wehner, J. Küppers (to be published).