

Promotion of catalytic reactions by depopulation of surface states

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Dissociative adsorption is the rate-determining step in many catalytic reactions. However, the promoting mechanisms for dissociative adsorption are not yet fully understood. It is shown here that electronic surface states influence the physisorption potential as well as the dissociation barrier. Additives are able to shift and populate or depopulate surface states. Consequently, dissociation is inhibited or promoted, respectively. The present model provides a consistent explanation for several experimentally observed promoting and poisoning effects in dissociative adsorption of molecules from the gas phase or from a physisorbed precursor state.

The dissociation of molecules is a rate-limiting step for many catalytic reactions. Therefore, the promotion of dissociation reactions has been one of the central research areas of surface science during the past decades. Despite enormous efforts the present understanding of promoter-enhanced dissociation is still far from complete.

The most extensively studied promotion mechanism is based on the local interaction between the promoter and the molecule that is to be dissociated; for example, a CO molecule coadsorbed with an alkali atom. Both the electric field set up by the alkali-induced surface dipole and the charge accumulation in the immediate vicinity of the adsorbed alkali atom favor an enhanced back donation of charge into the C-O antibonding $2\pi^*$ orbital. Feibelman and Hamann,¹ as well as Holloway and co-workers,² pointed out that the alkali-induced field is screened out by the substrate electrons over a rather short distance. Basically, only nearest-neighbor sites are notably affected by the additive-induced field. As such a local interaction cannot explain the—often sizable—promoting effect of very low additive concentrations, alternative, nonlocal mechanisms have been looked for.

A complementary mechanism emerged from research on the dissociation of oxygen on silver surfaces.^{3,4} In this case the dissociation is initiated by electron tunneling from the substrate Fermi level into the oxygen π_g antibonding orbital, as the molecule approaches the surface. Adsorption of alkali metals decreases the work function, which brings the Fermi energy E_F closer to the vacuum energy E_{vac} . This facilitates charge transfer and increases the dissociation probability. Vice versa, electronegative adsorbates inhibit the dissociation. At a given position of the antibonding affinity level the tunneling probability depends on the work function of the substrate, which is a global quantity. Accordingly, the enhancement of the electron tunneling from the substrate to the adsorbate is a nonlocal promotion mechanism.

Both models discussed so far fail completely when applied to the dissociation of H_2 . Recent experiments have convincingly demonstrated a poisoning effect of alkali metals⁵⁻⁷ and a promoting effect of oxygen⁶ on the dissociation of H_2 at various metal surfaces. This is in striking contrast to the models presented above and requires a different explanation. The barrier for dissociation is determined by the balance between the attractive branch of the chemisorption and the repulsive branch of the physisorption potential.⁸ The

barrier can be reduced by either increasing the attraction in the chemisorption potential⁹ or decreasing the repulsion in the physisorption potential. Brown, Luntz, and Schultz (BLS)⁵ pointed out (see Fig. 3 of Ref. 5) that the repulsive potential, and therefore the dissociation probability, is related to the asymptotic charge density (ACD) outside the metal surface in the following way: As soon as the charge clouds of an adsorbate and the substrate begin to overlap, the Pauli exclusion principle forces the kinetic energy of the electrons to rise steeply. This is the origin of the—extremely short range—repulsive part of the physisorption potential. A rapid falloff of the charge density implies a late onset of the repulsion for the incoming molecule. The molecule is then able to approach the surface up to a distance where the van der Waals attraction reaches appreciable values and becomes strongly physisorbed. In contrast, a charge density leaking out far into the vacuum causes an early onset of the repulsion and weak physisorption. By the same token, for a given chemisorption potential the transition barrier into a dissociatively chemisorbed state will be low in the former and high in the latter case. Assuming that the electrons leak out further into the vacuum, if the work function is small, while a large work function confines the electrons close to the surface, Brown, Luntz, and Schultz⁵ were able to explain the poisoning effect of alkali metals and the promoting effect of oxygen by the associated work-function change. The strong poisoning effect of low alkali-metal coverages for H_2 dissociation on Pt(111) (Ref. 5) and on Ni(111) (Ref. 6) can be described reasonably well in this model.

However, some recent results on the H_2 dissociation kinetics deviate severely from the work-function dependence predicted by the BLS model. For instance, a comparison of the H_2 dissociation on the fcc (111) surfaces of the late transition and the noble metals revealed an anomalous behavior of the Pd(111) surface, which exhibits a precursor-mediated, nonactivated adsorption path in contrast to all the other (111) surfaces.⁷ This behavior cannot be correlated with the work function. Furthermore, the modification of the H_2 sticking probability by potassium adsorption differs widely for different substrates despite a qualitatively similar work-function reduction: An extremely long-range poisoning is observed for K/Pt(111) (Ref. 5) and K/Ni(111);⁶ on Cu(110) potassium acts even as a promoter for H_2 dissociation,¹⁰ while on Pd(110) potassium causes short-range poisoning due to

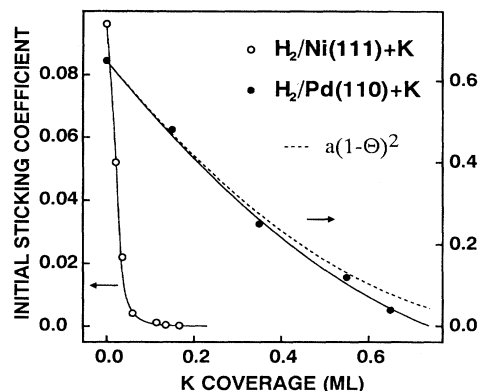


FIG. 1. Potassium-induced inhibition of H_2 dissociation on Ni(111) and Pd(111), respectively. On Ni(111) K has a long-range effect, while on Pd(111) the K-induced decrease of the initial sticking coefficient can be modeled by a pure short-range site blocking (dotted line). Both results are obtained with a H_2 beam energy of 70 meV (Refs. 6 and 7).

simple site blocking⁷ (see Fig. 1). The results can be accounted for, however, if the evanescent decay length of the charge density is considered in more detail. In many cases the ACD is controlled by surface states, which in turn can be modified by dopants. The modifier-induced shift and the accompanying population or depopulation of surface states accounts surprisingly well for the observed promotion and inhibition effects in H_2 dissociation, as we show in the following.

Invoking the Tersoff-Hamann theory,¹¹ on the one hand, and relying on experimental results, on the other, we have shown in a recent study¹² that Shockley surface states make a dominant contribution to the asymptotic local density of states at E_F on the fcc (111) faces of the d^9 transition metals Ni, Pd, and Pt and the noble metals Cu, Ag, and Au. With the exception of Pd, all of these surfaces exhibit a Shockley surface state at $\bar{\Gamma}$ in the center of the surface Brillouin zone (SBZ) close to the Fermi level. It fulfills all the Tersoff-Hamann criteria and therefore yields a sizable contribution to the ACD. As the bulk sp states exhibit a gap around E_F in the center of the SBZ, the surface-state contribution is in fact unrivaled. Pd(111) forms an exception, because the bulk band gap and the corresponding surface state lie entirely above E_F . According to the present model, the differences in the electronic structure result in a different physisorption potential. The shape of the physisorption potential can be characterized by the depth of the physisorption minimum, as inferred, for example, from the adsorption enthalpy of Xe, and by the height of the activation barrier for H_2 dissociation. The theoretical expectations are fully confirmed by the experimental evidence: While Ni, Pt, Cu, Ag, and Au behave rather similarly with respect to Xe adsorption and H_2 dissociation, Pd forms the big exception. On Pd(111) the adsorption enthalpy of Xe is about 30% larger than on the other (111) faces. The H_2 dissociation proceeds via a nonactivated, precursor-mediated channel in contrast to all other (111) surfaces, where the dissociation is strongly activated. Thus, Pd is a strong physisorption substrate, because it has no occupied surface state at the center of the SBZ and therefore the

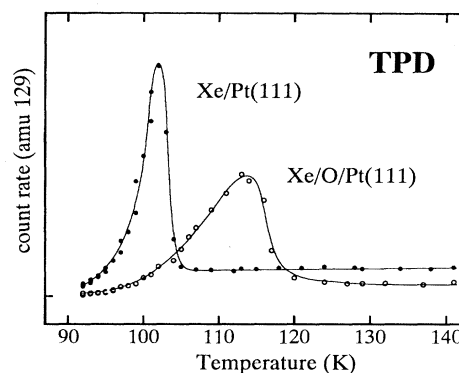


FIG. 2. Temperature programmed desorption spectrum of Xe from Pt(111) and Xe from Pt(111)- $p(2 \times 2)$ O. On the oxygen exposed Pt(111) surface the surface resonance is depopulated (Ref. 12), which increases the Xe adsorption enthalpy. The temperature scale has been calibrated by comparison with Ref. 31.

onset of the Pauli repulsion is delayed. A recent low-energy electron diffraction analysis of Xe on Pd(111) and Pt(111) (Ref. 13) lends further support to this conclusion: On Pd the Xe-substrate layer distance was found to be 0.7 Å smaller than on Pt.

The influence of surface states on the physisorption potential is also indicated by the effect of additives. We have shown in Ref. 12 that oxygen quenches the surface resonance at $\bar{\Gamma}$ on Pt(111). The temperature-programmed desorption spectrum of Xe from Pt(111) shown in Fig. 2 exhibits indeed a notable shift towards higher temperatures on the oxygen predosed surface in agreement with our model. Similarly, the reduction of the ACD due to the depletion of the surface state should also give rise to an increased H_2 dissociation probability. Although no data are available for Pt(111), the prediction can be tested on Ni(111). Panel (a) of Fig. 3 shows the position of the Ni(111) surface state as a function of O coverage¹⁴ as determined by inverse photoemission (IPE). On the clean Ni(111) surface the surface-state band shows up by its unoccupied tail just at E_F . With increasing O coverage the surface state shifts upwards and at an exposure of ≈ 3.8 L (1 L = 10^{-6} torr s) it appears clearly separated from E_F . At 6.8 L a $p(2 \times 2)$ structure corresponding to $\frac{1}{4}$ ML is observed. Accordingly, 3.8 L (roughly $\frac{1}{8}$ ML) is needed to completely depopulate the surface state. Figure 3(b) shows a measurement of the H_2 initial sticking coefficient (which, at the given temperature, is equivalent to the dissociation probability) on O promoted Ni(111).⁶ The sticking coefficient increases precisely up to a coverage of $\frac{1}{8}$ ML. A further increase of O coverage does not change the occupancy of the surface state and no further promotion is expected. Rather, the ordinary site blocking effect of O takes over and reduces the sticking probability to zero at O saturation. The striking agreement between the coverage where a complete depopulation of the surface state is observed, and the coverage where the promoting effect reaches its maximum strongly supports the proposed promotion mechanism involving the depopulation of the L_{2z} -derived surface state.

The model may be tested further by investigating the effect of alkali metals on the H_2 dissociation. Generally, the

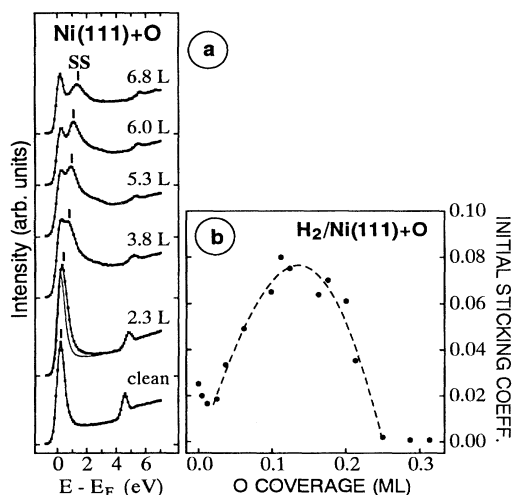


FIG. 3. The correlation between the oxygen-induced surface-state energy shift and the promotion of H_2 dissociation on Ni(111). Panel (a) shows the O-induced upward shift of the Shockley surface state on Ni(111) as observed in inverse photoemission (Ref. 14). Panel (b) shows the O-induced enhancement of the H_2 sticking coefficient at O coverages up to $\frac{1}{8}$ ML and the subsequent decrease, which can be attributed to site blocking (Ref. 6).

energy of surface states is lowered by adsorbed alkali metals^{15–20} as shown in the left panel of Fig. 4. The alkali metals increase the surface-state population and enhance the ACD, thus poisoning the H_2 dissociation. Even more specifically, as the stabilization of the surface states is a long-range effect, it should be observed already at very small alkali coverages. Figure 1 shows the poisoning effect of K on the H_2 dissociation for Ni(111).⁶ A similar result was obtained by Brown, Luntz, and Schultz⁵ on Pt(111). The quenching of the H_2 dissociation by K is exceedingly strong and provides clear evidence for a long-range effect. Even a site-blocking mechanism with 20 sites being blocked by a single K atom fails in modeling the precipitous decline of the dissociation probability with increasing K coverage.⁶

So far, we have considered the reactivity of the fcc (111) surfaces, where an occupied surface state dominates the ACD. One might ask now whether the influence of surface states can be detected on other surfaces as well. On the fcc (110) surfaces the $L_{2'}$ -derived surface state is found at the \bar{Y} point of the SBZ, i.e., at the zone edge. Thus, it does not entirely comply with the Tersoff-Hamann rules and should have a shorter evanescent decay length. However, the vacuum tail of the total charge density is also rather short on this surface due to the Smoluchowsky effect. Thus the electronic spillout is generally small on fcc (110) surfaces and the surface state may still contribute significantly to the ACD despite its relatively moderate decay length. In order to test this idea one may compare the H_2 dissociation probability on K modified Cu(110) (Ref. 10) and Pd(110).⁷ On Cu(110), room-temperature adsorption of K leads to a (1×2) reconstruction, i.e., the K atoms replace Cu atoms and form a surface alloy.²¹ As a consequence, the occupied Shockley surface state is shifted upwards and depopulated^{16,22} as shown for the similar system Na/Cu(110) in Fig. 4 (right

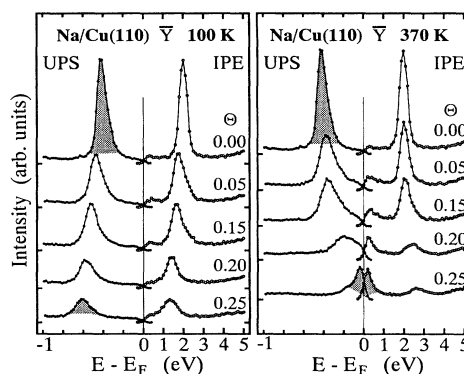


FIG. 4. The alkali-metal-induced shift of surface states on Cu(110). Left: Alkali-metal adsorption on the unreconstructed surface shifts the surface states downwards. Right: Substitutional alkali-metal adsorption on the reconstructing surface shifts the surface states upwards. At a Na coverage of $\frac{1}{4}$ ML the originally occupied surface state is almost completely depopulated (Ref. 16).

panel). According to the present model, this reduces the ACD and the H_2 dissociation should be promoted. This is exactly what was observed by Hayden and Lamont.¹⁰ In contrast, on Pd(110) the surface state remains unoccupied, no matter how the surface is prepared. The experimental results are again in perfect agreement with expectation: K adsorption has no electronic effect at all on the H_2 sticking coefficient. The observed reduction of the sticking coefficient is very well described by a simple short-range site blocking, i.e., a purely steric effect as shown in Fig. 1.

The K/Cu(110) system is peculiar in that here the H_2 dissociation is promoted rather than poisoned in contrast to all the other K-doped systems measured so far. We have attributed this promoting effect to the upshift of the Shockley surface state, which in turn is caused by the *substitutional* adsorption of the alkali metal. The surface state is destabilized, because in the reconstructing case a weakly attractive alkali atom is *substituted* for a substrate atom. On a nonreconstructing surface the alkali atom is *added* and the additional bonding interaction stabilizes the surface state as seen in Fig. 4.¹⁶ Therefore, alkali metals are able to destabilize or stabilize surface states, depending on whether they are substitutionally adsorbed or not. As a result, they can act as promoters for dissociative adsorption in the former case, while they can be efficient (long-range) poisons in the latter case. An upshift of electronic states resulting from substitutional adsorption has also been observed by Heskett *et al.*²³ on Na/Al(111) (although it was realized only in subsequent experiments that substitutional adsorption takes place). One might argue that the substitutional adsorption of alkali atoms on the more tightly packed surfaces will rarely occur and therefore an alkali-metal-induced promotion according to the proposed mechanism is a rather special case. Recently, however, reports about surface alloy formation on fcc (111) (Refs. 24–26) and fcc (100) (Refs. 27–29) faces are accumulating. As catalyst preparation usually involves a high-temperature treatment, it appears quite likely that surface alloy formation takes place more often than not. Interestingly, the alkali-induced bond weakening on chemisorbed molecules discussed in the Introduction is likely to be weaker in

the case of substitutional adsorption, because the electric field is better screened than upon normal adsorption. Thus the two promotion mechanisms behave conversely with respect to the alkali adsorption geometry.

The present model is in some aspects closely related to the BLS model. The essential new feature is the important role played by the surface states in building up the ACD. This allows a consistent explanation of the available experimental results on alkali-metal and oxygen promoted and inhibited H_2 dissociation, which is not possible using the work function as the relevant parameter. Obviously, the present mechanism cannot be invoked for the dissociation of chemisorbed molecules. The mechanism is only applicable to dissociation directly from the gas phase or out of a physisorbed precursor. It is, however, not particularly sensitive to the electronic structure of the dissociating molecule. Therefore it is likely to apply not only to H_2 , but also to several other molecules, where the high energy of the lowest unoccupied molecular orbitals prevents a facile population. It could, for instance, also explain the alkali-metal-induced promotion of N_2 dissociation, which is still a matter of controversy.³⁰ Another question is the relevance of the present mechanism for real catalysts, i.e., highly dispersed metal particles. One

should note, however, that the (111) surface is the most stable one for the fcc metals, therefore providing the largest surface area in small-particle systems. Thus we believe that the present discussion is highly pertinent even as far as real catalysts are concerned.

In summary, we present a complementary model for the promotion of dissociative reactions. It applies to dissociation directly from the gas phase or out of a physisorbed precursor. It is based on our previous observation that surface states contribute significantly to the asymptotic charge density. Additives give rise to an energetic shift of the surface states. A depopulation of the surface states reduces the ACD and consequently the barrier to dissociation. A stabilization of the surface states, in contrast, increases the ACD and poisons dissociative reactions. Within the present mechanism alkali metals can play a dual role as promoters or poisons, depending on whether they are substitutionally or regularly adsorbed.

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