Role of Steps and of Terrace Width in Gas-Surface Interaction: $O_2/Ag(410)$

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We demonstrate by vibrational spectroscopy that open steps are the active site for O_2 dissociation on Ag(410), and that the barrier to adsorption at defects can be measured by energy and angle resolved investigation of the dynamics of the gas-surface interaction. We identify a molecular adsorption channel with considerably reduced activation barrier and a nonactivated dissociative pathway. The O_2 sticking probability is increased at steps and strongly reduced at terraces with respect to Ag(100), implying that reactivity is influenced by terrace width.

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Industrial catalysts consist of a highly dispersed state of small particles with a large concentration of defects, such as facet edges between intersecting planes and steps. Although defects are known to play a pivotal role in determining both the dynamics of the gas-surface interaction as well as the overall reactivity for several systems [1–3], the surface science studies of model catalysts focused thus far on the low Miller index planes, which are rather unlike real catalysts. This gives rise to a shortcoming of the surface science approach to catalysis known as structure gap. The role of defects was addressed in detail only recently: For Ru(0001) it was shown that atomic steps are the only active sites for the NO and N_2 bond dissociation [4–6] and that steps are at least 10^9 times more reactive towards N_2 than terrace sites [6]. In other experiments, defects were induced by ion bombardment, and large effects were found, e.g., for NH_3 dissociation on Ru(0001) [7] and for O_2 dissociation on Ag(001) [8]. For the latter system, partial dissociation occurs at temperatures at which only admolecules are stable on the flat surface. This result is in accord with our previous suggestion [9] that kinks at steps are the active sites for O_2 dissociation on Ag(100), but it does not allow one to identify the active site unambiguously as a large variety of defects is produced by sputtering. A more rational approach to understand the role of defects is to investigate the dynamics of gas-surface interaction for stepped surfaces, which are characterized by a high density of a single, well-defined defect [10,11]. For $O_2/Pt(533)$, the (100) steps were demonstrated, e.g., to dominate the conversion from physisorbed into chemisorbed precursors, the barrier on Pt(111) being substantially higher [11].

In the present Letter, we show an energy and angle resolved experiment on the interaction of O_2 with Ag(410), a vicinal surface of Ag(100) characterized by an open step every fourth row of atoms. The (410) plane is the most intriguing among the (100) vicinal surfaces because it forms naturally when exposing Ag(100) to massive oxygen doses [12]. The experiments are performed in an ultrahigh vacuum apparatus equipped with a supersonic molecular beam and a quadrupole mass spectrometer (QMS) not in line of sight with the surface [13], which allows one to measure the sticking coefficient with the retarded reflector method of King and Wells (KW) [14]. The final adsorption state of oxygen is characterized by high resolution electron energy loss spectroscopy (HREELS). Spectra are recorded in-specular at 60° incidence and 1.7 eV electron energy. The Ag sample is a 7 mm diameter disk oriented within 1° with the (410) plane. Its surface is prepared *in situ* by sputtering and annealing to a crystal temperature, T, of 700 K until a good quality pattern is observed by low energy electron diffraction. The supersonic molecular beam is collimated to a spot diameter of 2 mm at the crystal for KW experiments. The translational energy, E_i, of the impinging molecules is varied by heating the ceramic nozzle and by seeding O_2 in He. The energy resolution of the beam is $\pm 10\% E_i$.

The surface geometry (see inset of Fig. 1) consists of three-atom-row wide (100) terraces and (110) steps. The angle of incidence of the impinging molecules, θ, is measured with respect to the surface normal. As the scattering plane is aligned across the steps and the surface forms an angle of 14° with the (100) terraces, $\theta = \theta_t = -14°$ and $\theta = \theta_s = +31°$ correspond to dosing normally to the terraces and to the step heights, respectively.

In Fig. 1 we show QMS traces of the O_2 partial pressure in the main chamber for KW measurements performed with $E_i = 0.97$ eV at two different angles. In both cases the molecules hit the terraces at 45°, but they impinge normal (solid line) and grazing (dashed line) to the step heights, respectively. At time t_0 an inert flag, intercepting the beam in the main chamber, is removed and the supersonic beam strikes the surface. The relative drop in the QMS signal is a direct measurement of the sticking coefficient. The initial value, denoted by S_0, is particularly important since it corresponds to the interaction with the bare surface. The experiment shows that S_0 is much larger when the step height is exposed than when it is in the shadow (0.42 against 0.07). Notably, at $E_i = 0.97$ eV and $\theta = 45°$, S_0 reads 0.35 for Ag(100) [15], implying that the reactivity is increased at steps and strongly reduced at terraces. The former effect is expected because of the smaller

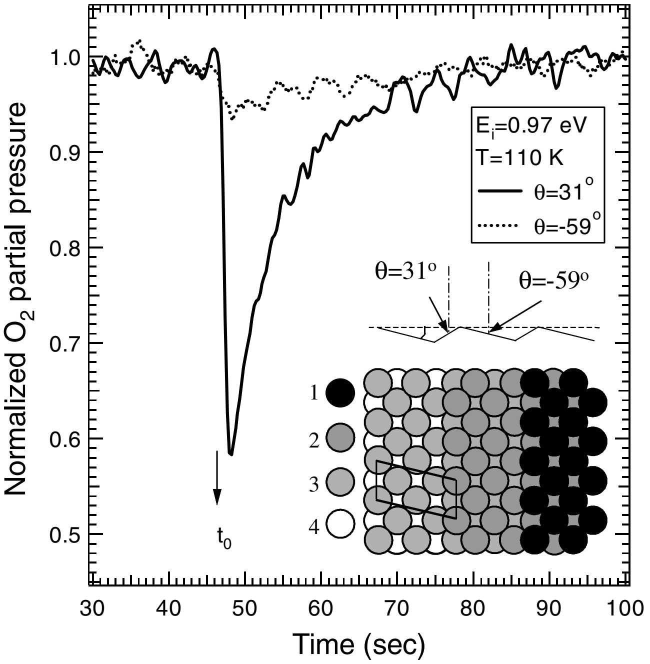

FIG. 1. KW traces for molecules impinging at $\theta = \theta_s$ and $\theta = -59°$. The Ag(410) geometry is reported in the inset.

coordination of step atoms. On the contrary, the reduced reactivity at terrace sites is connected to the limited terrace width and implies either a change of the electronic state of terrace atoms or their poisoning close to the step edges, i.e., a reduction of the effective terrace size. Assuming $S_0 = 0.07$ for the terrace atoms and weighting the difference between the two curves of Fig. 1 with respect to the projected terrace and step areas seen by the beam, we obtain $S_0 \approx 1$ for molecules impinging normally against the step heights.

The S_0 values, recorded at $T = 105$ K vs E_i, are reported in Fig. 2. In panel 2a, $S_0(E_i)$ at $\theta = 0°$ is compared with the corresponding curves for Ag(100) [15] and Ag(110) [16,17]. S_0 increases with E_i, indicating that O_2 adsorption is globally activated also in the presence of steps. Above $E_i = 0.2$ eV, S_0 is up to 30% lower than for the low index surfaces, in accord with the result for sputtered Ag(100) [18] and confirming that terrace sites are less reactive in the presence of steps. However, at variance with Ag(100) (inset of Fig. 2a), S_0 is still measurable with the KW method at $E_i = 0.09$ eV, showing the existence of nonactivated, defect related adsorption channels. Data recorded at other θ (see Fig. 3) indicate at this E_i only a weak angular dependence of S_0, with two maxima at $\theta \approx \theta_t$ and at large positive θ values. They are most probably associated to different mechanisms and their superposition causes the apparent minimum at $\theta \approx \theta_s$.

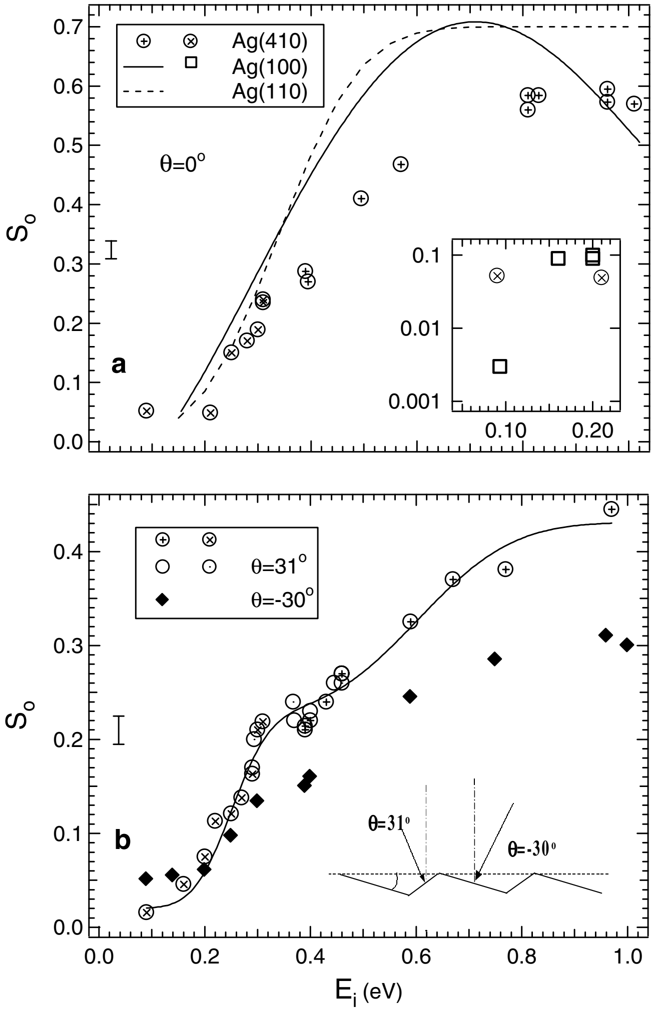

FIG. 2. S_0 vs E_i, at $T = 105$ K. (a) O_2 dosed at $\theta = 0°$; data are compared with results for Ag(100) and Ag(110). In the inset, "□" indicate data for Ag(100). (b) O_2 dosed at $\theta = -30°$ ($-16°$ off θ_t) and at θ_s [⊗: pure O_2; ⊕: seeded beam with 3.5% O_2; ○ and ⊙: other O_2 concentrations]. The error on S_0 is ±0.015. The continuous line is the best fit for $\theta = \theta_s$.

In Fig. 2b we compare the data recorded for $\theta = -30°$ and $\theta = \theta_s$. At both angles a plateau is present between $E_i = 0.3$ and 0.4 eV. The feature is particularly evident for $\theta = \theta_s$; this can be inferred also from the angular dependence of S_0 reported in Fig. 3, in which the difference between the curves of $S_0(0.39$ eV$)$ and $S_0(0.22$ eV$)$ is minimized around $\theta = 39°$.

HREEL spectra, recorded in the low coverage limit, are shown in Fig. 4. O_2 was dosed at $T = 105$ K and $\theta = \theta_s$ for different E_i. When dosing at high E_i, losses are present at 32–40 and 85 meV, while at low E_i only one loss (at ≈40 meV) is observed. The losses in the lower frequency range are caused by the adatom-surface vibrations at different sites [19], with only a minor contribution at 30 meV due to the admolecule surface stretch. The presence of significant intensity in this frequency range proves therefore that dissociation has taken place already at $T = 105$ K, contrary to what observed for Ag(100) and Ag(110). The pathway leading to dissociation is little activated or nonactivated, as the intensity is present at all E_i. This

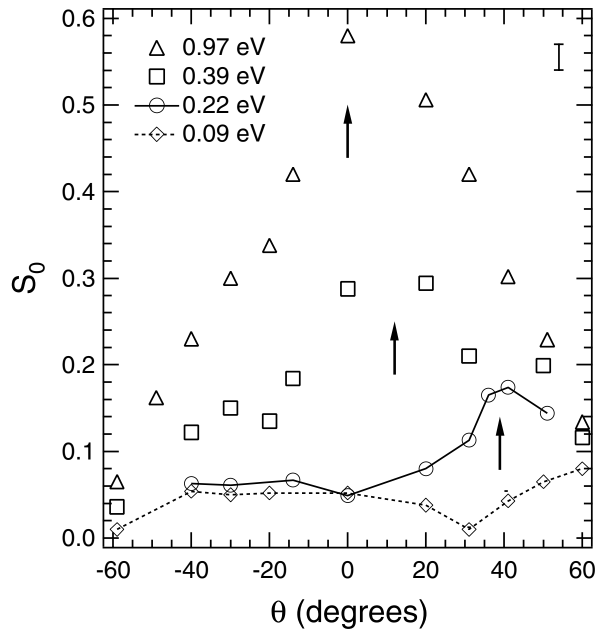

FIG. 3. S_0 vs θ, at $T = 105$ K and parametric in E_i. The arrows indicate the maximum of S_0 for different E_i.

observation is in agreement with the results for sputtered Ag(100) [8], for which, however, adsorption was not investigated at low E_i. The higher frequency loss is due to the internal stretch of adsorbed O_2. At low coverage, we observe this mode only for $E_i > 0.28$ eV, indicating that molecular adsorption results from activated pathways and that the anomalous increase of S_0 around 0.25 eV is connected to its onset at steps.

In Fig. 5 the temperature dependence of S_0 on Ag(410) is compared to the one of Ag(110) and Ag(100). $S_0(T)$ decreases smoothly, indicating that dissociation dominates over desorption when the admolecules become unstable ($T > 150$ K). For $T > 350$ K, the residence time becomes comparable to the one necessary to search for the active site by diffusion, and the decrease of S_0 becomes steeper than for Ag(110).

The energy dependence of S_0 is usually described by the error function (erf) with E_B and W (average height and width of the adsorption barrier distribution) as free parameters [17]. While for Ag(100) [15,20] and Ag(110) [17,20] a fit with a single erf was possible, this is no longer the case for Ag(410). Forcing a fit with a single erf, we obtain, for $\theta = 0°$, $E_B \approx 0.37$ eV and $W \approx 0.25$ eV. E_B compares well with the value it has for O_2/Ag(110) and O_2/Ag(100) while W is larger, indicating that less activated channels are present. The fit is improved adding one additional barrier with an average height of 0.25 eV. Since the latter is not present on defect-free surfaces, it must be associated to the O_2 interaction with open steps. At higher E_i, S_0 increases further because the O_2 molecules adsorb also at terraces. For $\theta = -30°$ the two barrier distributions are less separated. Since the data do not scale with total energy, an up-shift of the apparent position of the additional barrier is in fact expected.

The O_2 internal stretch energy on Ag(410) is 85 meV, independently of E_i. This result indicates that only one O_2 moiety forms on this surface, at variance with Ag(100) and Ag(110) where two O_2 species, vibrating at 79 and 84 meV, are present [21,22]. The absence of the 79 meV moiety on Ag(410) indicates either that it is destabilized

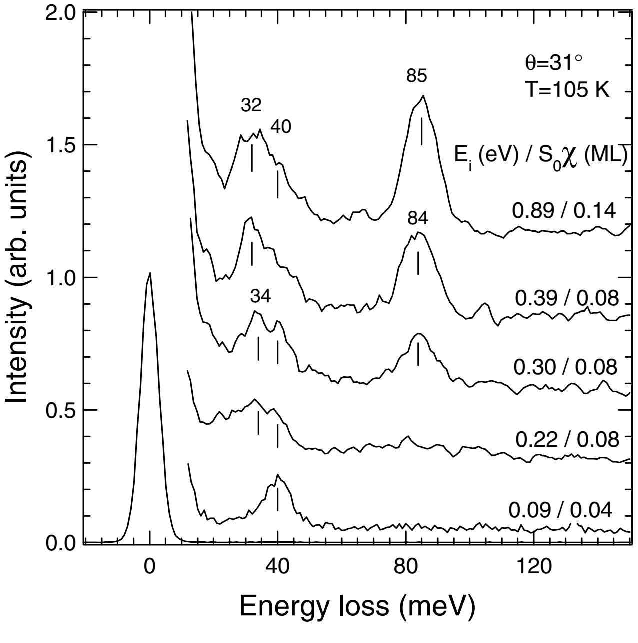

FIG. 4. HREEL spectra recorded after O_2 adsorption at $T = 105$ K, at θ_s and for different E_i. Only dissociative adsorption (peaks in the range 30–40 meV) is present at the lowest E_i, while admolecules (peak at 85 meV) adsorb for $E_i \geq 0.30$ eV. The O_2 dose, χ, in the central spectra was chosen in order to keep $S_0\chi$ constant. The magnification factor is 100.

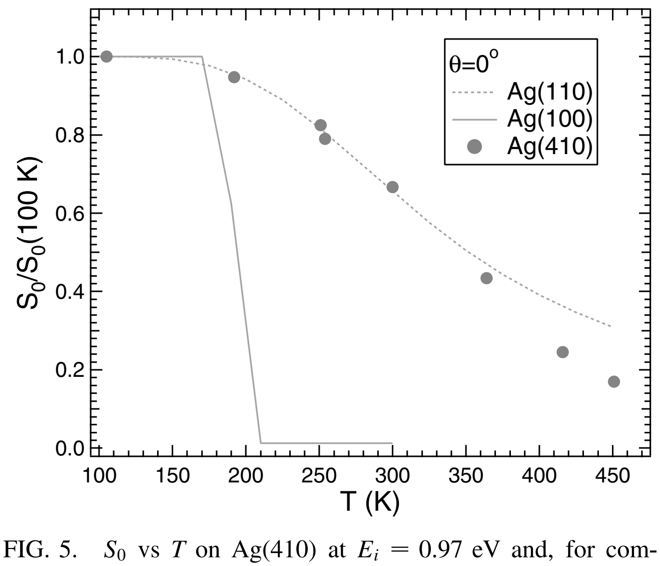

FIG. 5. S_0 vs T on Ag(410) at $E_i = 0.97$ eV and, for comparison, on Ag(100) (solid line) and Ag(110) (dashes) at $E_i = 0.39$ eV. The curves are normalized at $T = 100$ K.

by the limited terrace width or that migration towards the steps occurs in the 20 min needed to record the HREEL spectrum. The stretch energy of 85 meV would then correspond to admolecules decorating the step edges. The latter hypothesis is not unreasonable as theoretical calculations for $O_2/Ag(110)$ [23] show that O_2 prefers to sit in the grooves and maximize the number of bonds with Ag atoms. However, also the active site for dissociation must be at the step. As the molecular species is relatively stable, the molecular adsorption site and the dissociation site must be well separated by a potential energy barrier. One possibility is that the latter site is at the upper side of the step, as reported recently for $O_2/Pt(111)$ by scanning tunneling microscopy [24], while admolecules sit at the lower side of the step.

A possible objection to our work is that defects other than open steps might be responsible for the observed phenomena. In particular, open steps could roughen as the kink creation energy is quite small. We are confident that this is not the case: (i) S_0 decreases with T (see Fig. 5), while it would be expected to increase if the formation of the active defect were thermally activated; (ii) the loss intensity of atomic oxygen after a given O_2 exposure is similar to the one found on heavily sputtered Ag(100) [8,18], thus implying also a comparable concentration of defects. Clearly, this estimate is reasonable only for the density of the main defect, i.e., of open steps. We notice, moreover, that kinks at open steps form (111) microfacets, which are expected to be less reactive than the open step site itself.

Finally, let us mention that density functional theory finds no barrier for O_2/Ag [23,25]. The disagreement with experiment is explained with the difficulty for the molecules to switch, in the absence of defects, from the physisorption to the chemisorption diabatic potential energy surfaces [25]. Our data cannot prove this, but indicate that at defects the barrier is significantly reduced for molecular and vanishing for dissociative adsorption.

In conclusion, we have shown by KW investigations and by vibrational spectroscopy that open steps are the active site for O_2 dissociation on the otherwise inert (100) planes. Molecules hitting directly against the step edge can dissociate already at low translational energy, as the barrier for adsorption along this pathway is strongly reduced or even eliminated. At higher impact energies, we observe the onset of nondissociative adsorption, first at steps and then at terraces. Our data allow one to determine for the first time the activation barrier associated with a well-defined defect and demonstrate that it can be significantly reduced with respect to the low index surfaces [$E_B \approx 0.25$ eV, vs 0.37 eV for Ag(100) and Ag(110)]. Moreover, while step atoms are more reactive than atoms on Ag(100), as expected because of the smaller coordination, we find that the reactivity of terrace atoms is reduced, thus demonstrating that it is influenced by the limited terrace width. We expect these phenomena to be quite general and important for catalytic reactions where the adsorption of one of the reactants is strongly activated, so that adsorption at minority sites determines the overall reaction rate.

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