Gas–Surface Interactions

Stereodynamic Effects in the Adsorption of Ethylene onto a Metal Surface**

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The role of molecular alignment of nonpolar molecules in gas–surface interactions has so far escaped direct experimental investigations. We have employed a novel technique to prepare highly aligned supersonic beams and we show that ethylene molecules that impinge on silver surfaces precovered with molecular oxygen as "helicopters" have a higher sticking probability than "cartwheels" (Figure 1). The sticking probability, *S*, of reactant gas-phase molecules impinging on a metal surface is a key parameter for the quantitative understanding of heterogeneous catalysis at the gas–solid interface. Herein we report the dependence of *S* on molecular alignment for ethylene, an apolar molecule, interacting with a metallic surface, specifically O-recovered Ag (001). The observed steric effect is large, thus strongly influencing adsorption. The study of such a prototype system is very important to clarify the dynamics in the entrance channels of the potential energy surfaces controlling the catalytic epoxidation of unsaturated hydrocarbons.

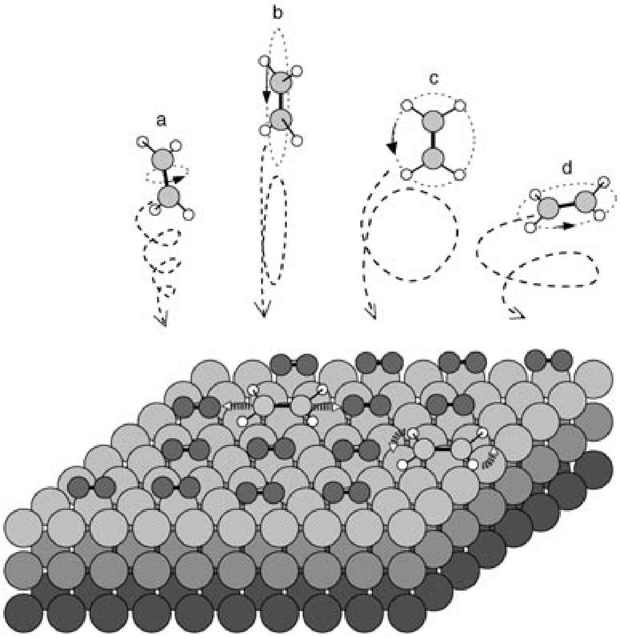

Figure 1. Ethylene molecules rotating along the principal axes impinge perpendicularly on Ag (001) metal surface precovered with O_2 and may stick in some favorable cases. A net variation of the coverage dependence of the sticking probability *S* when changing the geometry of approach of the C=C bond to the surface is observed: "helicopters" (d) stick better than "cartwheels" (b and c) or "cigars" (a).

Measuring *S* for a molecule in a well-defined quantum state represents a major goal of physical chemistry.[1] The extensive use of molecular beams in conjunction with the well-known retarded reflector method[2] allowed the determination of the dependence of *S* on translational energy and angle of incidence and on surface temperature and coverage for a wide set of gas–surface adsorption systems already in the first years of surface science.

However, the characterization of the dependence of *S* on the molecular internal state became accessible only recently, mainly as a result of the availability of high-power lasers, which allowed the preparation of molecules in well-defined

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[**] We acknowledge funding by INFM-PURS 1VA-2002 and PRIN 2003023939.

DOI: 10.1002/ange.200461302

rotational[3] and vibrational states.[4] Relevant information has been obtained by measuring the quantum state of molecules scattered off the surface and by applying detailed balance arguments.[5] The role of the spatial orientation of molecules impinging on a surface, or more specifically of the polarization of their rotational angular momentum *J*, has thus far not been investigated in much detail, even though the steric factor has often been addressed as a topic of fundamental interest.[6] The first investigations, performed by using electrostatic devices suitable to select which end of a polar symmetric top (A species showing two identical moments along two of the three principal inertia axes, one of which coincides with the molecular symetry axis) molecule hits the surface, shed light on the behavior of a symmetric NO-like species[7] and subsequently on polar polyatomic projectiles such as CH_3F[8] and ND_3.[9] Other methods to generate molecular orientation or alignment have been developed and include high electric or magnetic fields,[10a,b] polarized laser light,[10c] and intense nonresonant laser fields.[10d] Unfortunately, they work only for molecules that exhibit particular features, for example, large dipole moments or large polarizability anisotropies.

An alternative approach is based on the use of seeded molecular beams, for which the alignment of *J* is naturally generated by collisions during a supersonic expansion[11] and exploits the dependence of the resulting alignment degree on the final molecular speed.[12] This is a general phenomenon, as demonstrated by the study of a variety of molecules such as O_2 (paramagnetic),[12] N_2 (diamagnetic),[13] C_6H_6 (aromatic),[14] and very recently C_2H_2 and C_2H_4 (unsaturated aliphatic hydrocarbons).[15] For the lighter molecules, the experiments described above[12,13,15] suggest that: 1) When the nozzle source is operating at room temperature they are basically relaxed in the lowest rotational levels (essentially $J=1$ and 2). 2) The slow speed tail (ST) of the molecular beam velocity distribution (corresponding to velocities lower than 0.95 times the peak velocity) is essentially composed of molecules with an isotropic spatial distribution of *J*. In the language of angular momentum physics, such zero-alignment situations correspond to equally populated helicity states in which the helicity defines the projection of *J*, and indirectly also the orientation of the molecular rotational plane with respect to the molecular beam velocity direction. 3) The fast speed tail (FT) of the same velocity distribution (involving velocities larger than 1.05 times the peak velocity) consists of molecules with a high *J* alignment degree, that is, with marked nonstatistical helicity state population. Specifically, $85\pm10\,\%$ of molecules in the FT populate particular helicity states (zero helicity in the case of O_2, N_2, and C_2H_2).[16] The cited studies[12,13,15] also suggest that it is often sufficient to perform a proper velocity selection to control molecular speed and molecular alignment simultaneously, as also proved by recent gas-phase scattering experiments.[17]

Therefore, when the molecular beam impinges at normal incidence on the surface, as in the case of the present experiments with C_2H_4 (an asymmetric top molecule), FT essentially provides "cartwheels", molecules with their C=C bond rotating parallel to the molecular beam axis, whereas ST supplies about two thirds of "helicopters", that is, molecules with the C=C bond rotating perpendicularly to the beam direction.

In work described herein, the choice of the C_2H_4–Ag(001) system is motivated by a previous observation of a strong rotational dependence of the physisorption probability[18] and, even more importantly, by the fact that the ethylene–silver interaction is sufficiently weak so that steering effects are expected to play only a minor role. The well-known role of O_2 precoverage is to promote a measurable ethylene adsorption.[19,20] Chemisorption occurs in the π-bonded state, with an adsorption energy of ≈ 0.4 eV/molecule[21] and with the molecule lying flat on the surface.[20]

The Ag (001) single crystal was cleaned by following the usual procedure,[18] which consists of sputtering and annealing cycles to 700 K. The base pressure in the chamber reads 2×10^{-10} mbar and increases to 3×10^{-10} mbar when the supersonic beam is introduced. The uptake from the background is thus negligible during the timescale of the experiment. Aligned molecules in the FT, are separated from those statistically distributed, flying in the ST, by using a novel mechanical velocity selector (described in detail elsewhere[22]) positioned along the supersonic molecular-beam path, in the second stage of its collimation.[23] The beam flux is calibrated by a spinning rotor gauge and is corrected for the transmission of the velocity selector, which is measured by comparing the increase in the partial pressure caused by the unselected beam with that observed when selecting ST and FT. Notably, the angular divergence of the supersonic beam entering the ultrahigh-vacuum chamber is determined by the diameter of the collimators inserted along the beam path and reads 0.2°, thus ensuring the same beam intensity profile across the sample for ST and FT. Moreover, ST and FT experiments were performed with nearly identical fluxes. The diameter of the spot illuminated by the molecular beam is smaller than the sample diameter (10 mm), as determined by examining the ordered LEED (Low Energy Electron Diffraction) structures which form after exposing a clean Pd (100) sample to a supersonic O_2 beam seeded in He.

The upper panel of Figure 2 reports the backscattered C_2H_4 flux Φ versus time, measured by exposing the sample, at normal incidence, to a molecular beam of ethylene seeded in He (incident energy $E=0.36$ eV). The corresponding dependence of *S* on ethylene coverage (Θ_{Et}) which was obtained by integrating *S* over time and multiplying by flux, is shown in the lower panel. Uptake experiments were performed at $T=110$ K. The Ag (100) sample is precovered with a defined amount of O_2 prior to each ethylene uptake by dosing O_2 with a supersonic beam seeded in He. The O_2 coverage (Θ_{Ox}) can thus be accurately controlled and reproduced. The data reported in Figure 2 were obtained with $\Theta_{Ox}=0.03$ ML. The data obtained without the oxygen precoverage ($\Theta_{Ox}=0$ ML) are also reported in Figure 2 for comparison (shifted).

It is apparent from Figure 2 that: a) for the bare Ag (001) surface ($\Theta_{Ox}=0$ ML) there is no difference between molecules in FT and ST; b) for the O_2-precovered surface ($\Theta_{Ox}=0.03$ ML) the initial sticking probability increases, but does not depend on molecular alignment; c) with increasing C_2H_4 coverage, *S increases* for molecules in the ST but *decreases* for

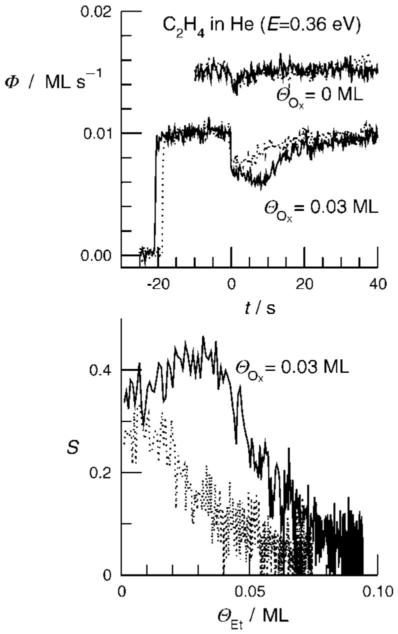

Figure 2. Scattered C_2H_4 flux Φ versus time (upper panel) and sticking coefficient S of C_2H_4 versus coverage Θ_{Et} (lower panel) on an Ag (001) surface precovered with oxygen ($\Theta_{Ox} = 0.03$ ML). Data are reported for the interaction of ST (continuous) and FT (dotted) of an ethylene beam seeded in He. The initial increase in the C_2H_4 flux corresponds to the introduction of the molecular beam into the ultrahigh-vacuum chamber, where an inert flag intercepts the beam to prevent it from hitting against the surface. When the flag is removed ($t = 0$), the scattered flux decreases owing to the gettering action of the surface of the crystal. The upper traces (shifted) in the upper panel show the results for the bare Ag surface ($\Theta_{Ox} = 0$).

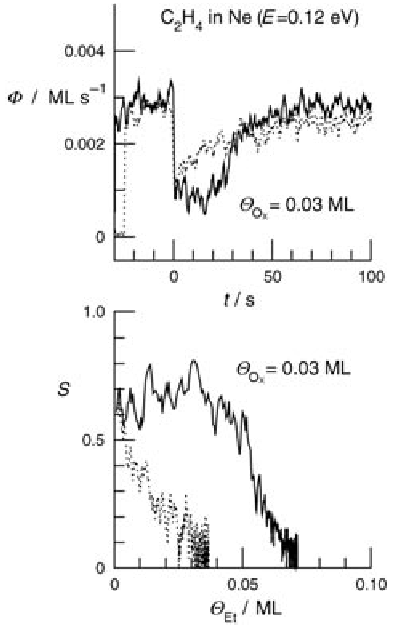

Figure 3. As in Figure 2, but for a molecular beam of ethylene seeded in Ne.

the FT. A large difference in S is already measured when selecting molecules in ST and FT with the ethylene coverage at only a few percent of a monolayer.

The difference in S between the two sets of velocity-selected molecules from the same molecular beam cannot be due to the small difference in translational energy, as demonstrated by performing the measurements at the same O_2 precoverage with ethylene seeded in Ne, for which the translational energy differs by a factor of three (Figure 3). The lower panels of Figures 2 and 3 shows that a qualitatively similar steric effect is found for the two very different incident energies. Moreover, the effect cannot be due to a possible change in the J distribution between ST and FT which would yield a lower average J, and hence a higher S, for FT molecules,[18] contrary to experimental evidence. We are therefore confident that the different behavior of ST and FT can only arise from the different degree of rotational alignment of the selected molecules. Points a) and b) clearly indicate that the interaction of incoming ethylene with bare silver atoms and with chemisorbed O_2 molecules is independent of the initial alignment of the incoming C_2H_4.

Point c) can only be accounted for if 1) ethylene molecules that are not scattered immediately after the first hit with the surface are temporarily trapped as a mobile and non-thermalized precursor with a memory of their initial alignment, and 2) "cartwheel" molecules in such a precursor state have a higher chance of being scattered back into the gas phase than "helicopters", when colliding with already chemisorbed flat-lying C_2H_4 molecules. The role of the mobile precursor is introduced to explain the strong dependence of S both with Θ_{Et} as well as with Θ_{Ox}. Because the ST and FT sticking curves already deviate at $\Theta_{Et} = 0.01$ ML, we deduce that the molecules in the precursor state "memorize" their initial rotational alignment for the time needed to explore a radius of some ten lattice spacings around the initial point of impact. When an ethylene in such a precursor state collides with a chemisorbed C_2H_4, it may be scattered off the surface with different probability, depending on the specific rotational mode involved.

In conclusion we have shown herein that a novel technique can be successfully applied to determine the role of molecular alignment in gas–surface interactions. We demonstrated that the steric effects can be quite large when interactions between transiently trapped and already chemisorbed molecules come into play, as is the case for the ethylene–Ag system reported herein. As hydrocarbon adsorption on metal surfaces often occurs through a precursor mechanism,[24] the present result may also be relevant for other adsorption systems. In fact, we have already observed similar alignment effects for propylene interactions with bare Ag (001), whereas no effect was observed for the more strongly bound O_2–Ag (100) and C_2H_4–Pd (100) systems in which σ bonding occurs.

Received: July 14, 2004

Keywords: heterogeneous catalysis · hydrocarbons · molecular beams · silver · surface chemistry

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