“Hot” Surface Activation of Molecular Complexes: Insight from Modeling Studies**
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The activation of gas-phase molecules on hot solid surfaces, a major issue for both fundamental research and technological applications, plays a key role in the fabrication of advanced materials supported on suitable substrates.\[1] The interest relates to the increasing requirement of attaining a deeper insight into the first molecular activation stages, a critical step in the bottom-up nucleation of functional nanostructures with specific size–structure relationships. While molecular activation is in general influenced by the surface chemical composition, in the harsh conditions typical of hot substrates, the surface–molecule energy transfer becomes crucial. As a consequence, physisorption competes with desorption, a diverse reactivity emerges, and novel activation mechanisms may be triggered, thus leading to products not attainable under mild conditions. Atomistic-level details of encounters between gas-phase molecules and hot surfaces are not easily available,\[2] owing to both the fast kinetics associated with high temperatures and the difficulties of performing experimental in situ analysis on a molecular scale. In this context, first-principles modeling studies\[3–5] are of significant relevance in the design and tailoring of specific molecular routes to functional nanosystems, such as chemical vapor deposition (CVD) processes, in which surface temperature is a decisive factor. Herein, we report on how the multifaceted dynamical behavior of a CVD precursor on a hot substrate, captured by simulation, disclosed a novel general activation channel for high-temperature surface processes: the fast rolling motion of vibrationally excited molecules. This surface mobility regime, never reported to date, combines fast lateral transport of an adsorbent with excitation of its internal modes, thus suggesting that energetic collision of rolling species is actually one of the ways through which molecules are activated and react at a hot surface.

Observations were collected in a computer experiment in which the Cu\(^{3+}\) complex [Cu(hfa):tmeda]\[6] (see Figure 1, left) was put in contact with a hot model surface (750 K). [Cu(hfa):tmeda] is a successful CVD precursor thanks to its favorable mass-transport properties and, in particular, to the fact that it sublimes without side decomposition. Yet the conversion of [Cu(hfa):tmeda] into Cu\(_2\)O systems evidences a temperature-dependent ligand elimination through molecular activation on the hot substrate, the exact mechanism of which is unknown to date. The solid-state Cu\(_2\)O nucleation occurs when [Cu(hfa):tmeda] (sublimated at ca. 343 K in a cold-wall CVD reactor) in O\(_2\)/H\(_2\)O-based atmosphere interacts with oxidized Si(100) heated substrates (523–823 K). Both the system structure and composition (CuO vs. Cu\(_2\)O) and its spatial organization (from continuous films to anisotropic quasi-1D nanowires) can be finely tuned through controlled variation of both reaction atmosphere and surface temperature.\[8a–d]

Under these conditions, the exposed substrate surface is a hydroxylated silica layer.\[1b,9] On this basis, the surface model used herein consists of a slab of amorphous silica approximately 1 nm thick, with a concentration of 2.8 surface silanol (Si–OH) groups per square nanometer (see Figure 1, right, and the Experimental Section). A [Cu(hfa):tmeda] molecule was positioned on top of such a surface. The system temperature was set to 750 K, and the time evolution was monitored by first-principles molecular dynamics (FPMMD) for a total of approximately 30 ps. The target molecule remained close to the substrate during the whole simulation, that is, with its closest contact with the surface atoms always within 2–3 Å (see Figure 2, left). Nevertheless, the complex cannot be considered as firmly physisorbed, as the time evolution of the \(x\) and \(y\) components of the Cu coordinates (Figure 2, right) indicates a remarkable mobility on top of the surface.

Three regimes were identified along the [Cu(hfa):tmeda]/hot surface simulation. In the first part of the trajectory (0–4 ps interval, region \(a\)), the complex diffuses over the surface through a series of small back-and-forth bursts, with a rocking motion. In such a slow “bump-and-rock” diffusion regime, favorable longer-lasting molecule–surface contacts may be established. Indeed, a low-mobility behavior is observed subsequently (4–20 ps interval, region \(b\)), in which the motion is confined to an area approximately 1 × 1 Å\(^2\) (highlighted in green in Figure 2,
The complex is localized in two small areas (ca. 0.25 /C1382 each). A closer inspection of this trajectory segment allows us to identify two subregions, b′ and b″ (inset, Figure 2), in which the complex is localized in two small areas (ca. 0.25 /C1382 each). This regime can hence be associated with two physiosorption events separated by a short site-to-site diffusion phase. Finally (20–30 ps interval, region c), a fast “roll-and-go” diffusion of the complex over the substrate takes place. In this high-mobility regime (see Figure 3 and movies in Supporting Information), the [Cu(hfa)₂tmeda] ligands change their mobility regime (see Figure 3 and movies in Supporting Information), the [Cu(hfa)₂tmeda] ligands change their mobility regime (see Figure 3 and movies in Supporting Information) and point to a general excitation of the molecular freedom, as clearly emerges from the time behavior of the mean square displacement calculated for the [Cu(hfa)₂tmeda] complex on top of the hot hydroxylated silica surface (black dotted line). msd(t) sections showing linear behavior versus time have been interpolated using a least-square fitting to msd(t) = A + Qt. In the linear segments in regions a and c (blue dashed lines), the values of Q/6 provide an estimation of the diffusion coefficient in these regions. The vertical dot-dashed lines mark the borderlines between the a, b, and c regimes.

The mean square displacement msd(t) = [(r(t)−r(0))²] calculated for the Cu atom along the trajectory (Figure 4) illustrates the differences in the aforementioned three regimes. In region a, a diffusive motion is detected, as indicated by the linear behavior of msd(t) versus t. [10] The diffusion coefficient of the complex on top of the hot surface is estimated to be approximately 0.4 × 10⁻⁷ m² s⁻¹ for such a regime. In region b, msd(t) shows two plateaus that can be associated with the two physiosorption events b′ and b″. Finally, in region c, characterized by high complex mobility, msd(t) shows a rapid increase. Correspondingly, a large diffusion coefficient (ca. 3 × 10⁻⁷ m² s⁻¹) has been estimated. It is worth pointing out that the high-mobility phase follows a labile physiosorption event, thus highlighting the relevance of energy transfer between the hot surface and the molecule in this context. Such a behavior is in line with the fact that kT (ca. 1.5 kcal mol⁻¹) is an appreciable fraction of the calculated complex physiosorption energy (5.0 kcal mol⁻¹).

Besides disclosing such rich and multifaceted dynamics, the simulation reveals that interaction with the hot surface strongly perturbs the [Cu(hfa)₂tmeda] internal degrees of freedom, as clearly emerges from the time behavior of the Cu–ligand (Cu–L) bond lengths (Figure 5). All Cu–L distances show pronounced oscillations,[11] the largest effects are detected for the weakest contact in the gas-phase molecule,[7] Cu–O₁, which elongates up to about 4 Å. In the physiosorption regime b, Cu–L bond distortion correlates with separation from the surface; for example, O₁*, which is closer to the surface than O₁, shows larger bond oscillations (Table 1). Therefore the complex loses its C₃ symmetry as a consequence of interactions with the hot surface, and the extent of symmetry breaking is more pronounced than for a 0 K surface (see Table 1). After approximately 13 ps, the oscillation amplitudes of all the Cu–L bonds undergo a non-negligible increase, which becomes remarkable in region c. This trend, where the Cu–O₂ distances transiently become even longer than the Cu–O₁ ones, gives evidence of the large structural distortions experienced by the molecule in the fast diffusion regime and points to a general excitation of the molecular internal modes. Interligand interactions, which are relevant for activation, are promoted as well. In particular, close contacts between tmeda CH₃ protons and hfa O₁ atoms (down to 1.73 Å; Figure 5 c) suggest a possible decomposition...
Experimental Section

The behavior of [Cu(hfa)2tmeld] on a model hydroxylated silica surface was simulated within density functional theory (DFT) using periodic boundary conditions and plane waves (PW) basis sets. The surface was modeled by periodically repeating a 1 nm thick slab of stoichiometry SiO2:H2O (with water dissociatively chemisorbed) and dimensions of 1.69 × 1.69 nm2. The simulation system, consisting of 185 atoms, was built by placing a [Cu(hfa)2tmeld] molecule on the model surface in a 1.69 × 1.69 × 2.6 nm3 simulation box. FPMD simulations were performed on this system with the CPMD code (www.cpmd.org). Ultrasoft pseudo-potentials were adopted for Cu, O, N, C, and H atoms, while a norm-conserving pseudopotential was adopted for Si. PW cut-off values were 30 and 240 Ry for the orbital expansion and electronic density, respectively. The Perdew–Burke–Ernzerhof spin density functional (multiplicity 2) was adopted. Benchmark calculations for this level of theory can be found elsewhere. A time step of 0.121 fs was used for the trajectory integration. The inertia parameter for the electronic coefficients was 500 au. After 5 ps equilibration, data were collected along a ca. 30 ps production run in the canonical ensemble using a target temperature of 750 K and Nose–Hoover thermostats. Geometry optimization was performed on the lowest-energy configuration sampled in the trajectory. The complex binding energy was calculated by subtracting from the energy of such an optimized configuration the sum of the energies of the optimized substrate slab and that of the isolated complex calculated in the same simulation box. Optimizations were performed using a quasi-Newton algorithm and a convergence criterion of 10−6 au as maximum force per atom. The calculated surface–[Cu(hfa)2tmeld] binding energy was 5.0 kcal mol−1.

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[11] The Cu–O and Cu–N stretching frequencies in the complex are below 600 cm⁻¹, see Ref. [7a], while at 750 K, $\frac{kT}{\hbar c} = 500$ cm⁻¹.


