Adsorptions- und Desorptionsdynamik
Gas-Surface Dynamics

direct scattering

trapping desorption

sticking

Pd(111) / CO
300 K

Pd(111) / He
300 K

T. Engel & G. Ertl, ~1980
He Beugung

rekonstruierte Au(111) Oberfläche

Manninen et al., 1982
Nicht-aktivierte Adsorption

Diagramm mit den folgenden Abschnitten:

(a) (b) (c) (d)

Energie- und Distanzverlauf von Chemisorption und Physisorption

Nonactivated adsorption

Chemisorption well

Physisorption well

Distance from Surface, z
Figure 8. Results for the probability of an atom losing an amount of energy $E$ when it has an initial kinetic energy $\varepsilon$, according to the forced oscillator model. Values chosen correspond to the collision between a hydrogen atom and an atom in a Cu surface in its ground vibrational state. For an initial kinetic energy of 0.5 eV, in addition to the inelastic peak centred at 0.03 eV there is an elastic component to the scattered distribution. For a greater initial kinetic energy (2.0 eV) the loss to the substrate is far in excess of the phonon band width, and appears as a Gaussian, centred on the classical value obtained using the binary collision model (equation 4.2) [86].

John Harris, 1991
For a radiationless transition of this character, certain conditions are necessary. There must be no change of total angular momentum, nor a change in the total spin vector, nor a change in the parity of the molecular term. For a molecule initially in a 'L state, these conditions will usually be satisfied. A hydrogen molecule, for instance, will dissociate at K into two atoms with opposite spins, and the parity of the states before and after the transition will be even.

A molecule approaching the metal with an energy W, insufficient to reach K, might, according to quantum mechanics, penetrate the harrier, but the probability is small unless W is very nearly of the same height as the point of intersection K. The height of K above the zero energy is in fact the ''energy of activation'' (P) necessary for a transition from the state (I) to the state (2). If the energy of the impinging molecule is large, the molecule will swing past K at considerable speed and the probability of a switch is again small. For the best chance of a transfer WJ...
“Since evaporation and condensation are in general thermodynamically reversible phenomena, the mechanism of evaporation must be the exact reverse of that of condensation, even down to the smallest detail”

I. Langmuir, 1916

• Mikroskopische Reversibilität: einzelne Trajektorie
• Detailed Balance: Reaktionsgeschwindigkeiten
Clausing Rules

- Der 2. Hauptsatz bedingt, dass die Verteilung der Teilchen, die die Oberfläche verlassen, durch $\cos \theta$ beschrieben wird.

- Das Prinzip des detaillierten Gleichgewichts verlangt, dass für jede Richtung und jede Geschwindigkeit gleich viele Teilchen emittiert werden, wie einfallen.

- Jede wohldefinierte kristalline Oberfläche hat einen Haftkoeffizienten kleiner als 1, der vom Winkel und der Geschwindigkeit abhängen mag.
Wenn \( T_s = T_g \), dann müssen allen Teilchenflüssen \( j_{in} \), entgegengerichtete Teilchenflüsse \( j_{out} \) gegenüberstehen.
Gasphase

Adsorption

Streuung

im Gleichgewicht

Desorption
Dissoziative Adsorption

H/Mg

Nørskov … Lundqvist, 1981
Understanding Heterogeneous Catalysis from the Fundamentals

Fig. 8.5. Variations in the O adsorption energy along the 4d transition metal series. The results of full DFT calculations are compared to those from the simple d-band model and to experiments. Below the same data are plotted as a function of the d-band center. From Hammer and Nørskov (2000).

Table 8.1

Parameters describing the electronic structure of the transition metals. From Ruban et al. (1997).

The trends for atomic oxygen along a series of 4d-transition metals (Fig. 8.5) illustrate the use of the d-band model. Both experiment and DFT calculations show that the bond gets stronger ($\Delta E_1$ more negative) towards the left in the Periodic Table. The same trend applies in the 3d- and 5d-series (Fig. 8.1). It is also the rule for a number of other adsorbates (Nilsson et al., 2005). These trends are described quite well by the d-band model with $\Delta E_1$ calculated with the Newns–Anderson model. Clearly they correlate...
Fig. 17. (A) and (B) show specimen trajectories with (A) largely reagent translation \( (T = 9, V = 0) \) and (B) largely reagent vibration \( (T = 1.5 \) and \( V = 14.5) \) on an “early barrier” surface, that is, type I. (C) and (D) show trajectories with (C) largely reagent vibration \( (T = 1.5 \) and \( V = 7.5) \) and (D) largely reagent translation \( (T = 16.0, V = 0) \). All energies are in kilocalories per mole; reagent vibration is relative to \( E(V = 0) \); the particles A, B, and C have equal mass. Positive and negative vibrational phases are shown with solid and broken lines, respectively. Barrier heights on both surfaces I and II are 7 kcal/mole; contours are labeled in kilocalories per mole. [Courtesy of The Journal of Chemical Physics (90)]
H$_2$/Cu

![Graph showing initial sticking probability vs. $E_1 \cos^2 \theta_1$ (eV)]

- Initial sticking probability for different temperatures: 2100 K, 1650 K, 1460 K, and 1170 K.
- Data points for pure D$_2$.
- Symbols indicating different incident angles: $0^\circ$, $30^\circ$, $45^\circ$, and $60^\circ$.

![Graph showing relative probability vs. kinetic energy (eV)]

- Relative probability plots for $D_2$/Cu(111).
- Curves for different vibrational states: $v=3$, $v=2$, $v=1$, and $v=0$.
- Kinetic energy range from 0.0 to 1.2 eV.
- Temperature curves for 120 K, 600 K, and 800 K.
H₂/Cu: Desorption

\[ N = \exp \left( \frac{E_a}{kT_s} \right) \]

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<th>( T ) [K]</th>
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<td>( \langle E_{\text{trans}} \rangle )</td>
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estimated from Michelsen, et al., JCP 98, 8294 (1993)
$\text{H}_2$/Cu: Isotopeneffekt