Heterogene Katalyse

- mikroskopisch -
“The reaction which takes place at the surface of a catalyst may occur by interaction between molecules or atoms adsorbed in adjacent spaces on the surface, ... or it may take place directly as a result of a collision between a gas molecule and adsorbed molecule or atom on the surface.”

Langmuir, 1941
Diffusion
Reaktion
Chemisorption
Desorption
Irvin Langmuir
1881 - 1957
Cyril Hinshelwood
1897 - 1967
The catalysis of the parahydrogen conversion by tungsten

By D. D. Eley and E. K. Rideal, F.R.S.

(Received 19 March 1941)

The parahydrogen conversion has been measured on a tungsten surface, as a function of the surface concentration of adsorbed oxygen, acting as a poison. This surface concentration was measured by a contact potential method. The oxygen would appear not only to cut down the fraction of surface available for reaction, but also to influence the reactivity of the neighbouring chemisorbed hydrogen. An important factor in this influence may be dipole-dipole interaction between the adsorbed atoms. A part at least of the oxygen adsorbed on tungsten can be removed at room temperature by reaction with hydrogen. Films of carbon monoxide, nitrogen and ethylene also poison the catalytic activity of tungsten and there is some

Generic Kinetics

- **Langmuir-Hinshelwood**

- **Eley-Rideal**

- [Diagram showing the relationship between $R_{LH}$ or $R_{ER}$ and $p_A$ (with $p_B$ held constant)]
CO\textsubscript{2} Formation

\[ \text{CO}_2 \text{ Formation} \]

\[ \begin{align*}
\text{Reaction Rate } r_{\text{CO}_2} & \quad [\text{rel. u.}] \\
\text{Temperature } [^\circ\text{C}] &
\end{align*} \]

\[ \begin{align*}
\text{Pt}(210) & \\
\text{Pd}(110) & \\
\text{Ir}(110) &
\end{align*} \]

\[ \begin{align*}
T = 500 \text{ K} & \\
P_{\text{O}_2} = 17 \times 10^{-6} \text{ mbar} &
\end{align*} \]
CO solo, Arrhenius Verhalten

O voradsorbiert, CO Strahl

pseudo 1. Ordnung

CO sucht Reaktionspartner

CO(g) + 0.5O₂(g)

259

Transition state

105

CO(ad) + O(ad)

ΔH_f = 283 kJ mol⁻¹

21

CO₂(ad)

CO₂(g)
CO(g) + $\frac{1}{2}$ O₂(g) → CO₂(g)

mit Katalysator

ΔE=500

ΔE=-284

~ -33

Einheiten kJ/mol
A year later, a study was reported translational energy depends on that of the incident molecule. In this study, HCl was observed in molecules. Highly vibrationally excited hydrogen molecules have been observed at the determination of internal state distributions of product cal measurements are required. The first such studies concerned ER mechanism for this elementary reaction. Conceptually relates the rate of reaction to the incident flux and to the surface.

Until relatively recently, the experimental evidence for the ER mechanism came largely from kinetic measurements, particularly the recent work of Jackson and Persson.

Very recently, Jackson and Persson have included rotational motion for the first time by performing 3-D quantum mechanical calculations, which clearly established that product distributions, quantum-state distributions have now been observed. Notice also that ER reactions are far more exothermic than their LH counterparts, with an excess energy from the reaction zone into the crystal more accurately.

For us, the working definition of an ER reaction is that it should occur before the reagents have become equilibrated to proceed with a very small activation barrier, consistent with the abstraction of halogens from Si(100) by incident H.

The low degree of energy disposal to the lattice.

Figure 9 shows the angle of the incidence beam (60°) is indicated graphically by the arrow. These results are attributed to an ER mechanism. The broken line corresponds to cos θ, which is expected in the absence of dynamical factors. The tics are placed at 10° intervals.

Figure 8. Polar plot of the angular distributions of the HCl product of the reaction of H atoms with Cl/Au(111) for T, = 100 K. (Signal intensities are proportional to the distance from the origin.) Results are displayed for incidence energies of 0.07 and 0.37 eV, as labeled. The angle of the incidence beam (60°) is indicated graphically by the arrow. These results are attributed to an ER mechanism. The broken line corresponds to cos θ, which is expected in the absence of dynamical factors. The tics are placed at 10° intervals.
\[ 0.5 \text{N}_2 + 1.5 \text{H}_2 \rightarrow 0.5 \text{N}_2(\text{ad}) + 1.5 \text{H}_2(\text{g}) \]

\[ \Delta H = 11 \text{ kJ mol}^{-1} \]

\[ \text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{ad}) \]

\[ \text{NH}_2(\text{ad}) + \text{H}(\text{ad}) \]

\[ \text{NH}(\text{ad}) + 2\text{H}(\text{ad}) \]

\[ \text{N}(\text{ad}) + 3\text{H}(\text{ad}) \]
Fig. 20. Comparison of calculated and measured ammonia production over a commercial iron-based catalyst for a broad range of temperatures, pressures, N/H ratios and gas flows.

High Miller indexed fcc surface with steps / kinks

BALSAC plot
\[ \Theta = 0.03 \text{ ML} \quad \Theta = 0.15 \text{ ML} \]
