

An introduction to molecular heterogeneous catalysis

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AN INTRODUCTION TO MOLECULAR HETEROGENEOUS CATALYSIS

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Abstract:

Fundamental concepts of heterogeneous catalysis are presented. Sabatier's principle relates *activity* with an *optimum* interaction energy between reactant and catalyst. Selectivity is determined by the *mechanism* of reaction and *surface state* of the catalyst. Surface reconstruction may lead to facetting of surfaces and non-ideal mixing behaviour of adsorbed surface layers. This may have large consequences for catalyst behaviour. Principles of chemisorption and dissociation will be highlighted.

1. A Summary of our Understanding of Surface Chemical Reactions

Catalysis has only recently started to outgrow the level of a purely empirical discipline. The reason for this slow change from "alchemy" to science is the complexity of practical catalysis as well as the complexity of the catalytic reactions. Several developments in the past two decades have led to a major advance in the knowledge of solid surfaces [1]. These developments are:

- Application of modern spectroscopic methods to the characterisation of solid state surfaces such as catalysts [2]. Catalysts are usually highly porous and high surface area materials. On the surface of the catalyst support, catalytically active compounds are distributed that are often ill defined and complex in composition.
- The study of single crystal surfaces under well defined conditions, made possible by the development of Ultra High Vacuum Technology.
- Application of molecular beam technology [3], in which the reactivity of small particles can be studied as a function of particle size.
- Computational chemical methods that enable predictions on the interaction energies and structure of intermediates in heterogeneous and homogeneous catalytic reactions [4].
- Advances in synthesis (manipulation of molecules) have led to techniques to fabricate well defined surfaces and model systems, so that theoretical insights can be implemented on a molecular level.

In this chapter we will focus our attention on the molecular basis of catalysis as a phenomenon in kinetics [5].

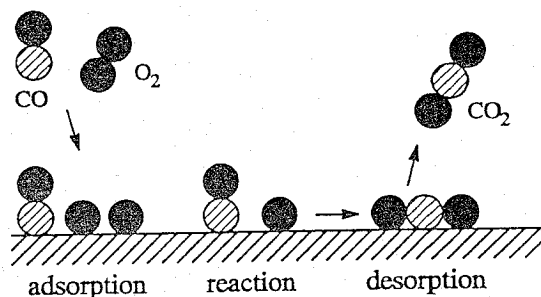


Figure 1. Schematic representation of the oxidation of CO.

The essence of a catalytic reaction is that it is a self-regenerating cycle of successive elementary reaction steps. The catalytically active site, free of reactants before reaction, is reproduced after the reaction. This is illustrated in Figure 1 with the example of the catalytic oxidation of CO. In this reaction scheme we discern four different elementary reaction steps. First the reactant molecules CO and O₂ have to adsorb on the surface (step 1: Adsorption). Then O₂ has to dissociate (step 2: Dissociation). In the third step an oxygen atom recombines with CO to produce CO₂ (step 3: Recombination). In a final step the CO₂ molecule desorbs and the free surface vacancy is regenerated (step 4: Desorption).

Most practical reactions are more complicated, since also surface diffusion and often surface reconstruction occurs. When there is no synergy between reactions on different sites, there is no correlation between the phases of the reaction cycles and the overall reaction is stationary, not showing oscillations on a macroscopic level. However, examples of cyclic surface reactions are known in which the cyclic nature of the total surface composition could be experimentally followed [6].

The example mentioned above can also be used to introduce the principle of Sabatier, which is the basis of catalytic kinetics. According to this principle the rate of a reaction is maximum for an optimum value of the interaction between adsorbate and catalysis surface. This stems from the competing nature of some of the different reaction steps that form the catalytic reaction cycle. In the case of the CO oxidation reaction, the elementary reactions that compete are dissociation and desorption.

When a weak interaction between reactant and surface is increased, the rate of dissociation will increase. This may occur by changing to a more reactive surface such as metal. However, when the interaction of reactants or products with the surface becomes too strong, no molecules will desorb and the surface becomes blocked by adsorbates. For the example of the CO oxidation reaction, chemisorbed CO will block the surface at low temperatures. Also

the interaction with oxygen may be too strong so that surface or bulk oxide formation may occur.

In the case of surface blocking by CO, a weaker interaction between CO and the surface will shift the equilibrium of absorbed CO, the surface coverage of CO will decrease, and the overall reaction rate will increase. The principle of Sabatier is illustrated schematically in Figure 2. The reaction rate has a volcano type dependence on the interaction strength of adsorbate and catalyst, a phenomenon that has been often observed experimentally. The reaction rate has a positive order in the reactant to the left of the maximum where the interaction strength is small. To the right of the maximum the reaction order becomes negative in reactant or product, because the surface sites become blocked by adsorbates. For the oxidation reaction of CO, platinum is one of the most effective catalysts.

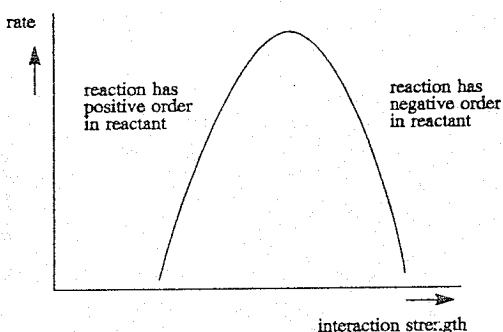
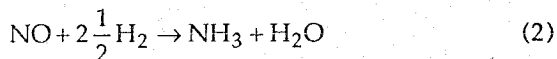
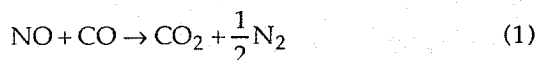


Figure 2. Principle of Sabatier

When more than one product is formed, the selectivity of the reactions is to be considered. We will discuss this qualitatively for the reaction of CO with NO in the presence of H₂, a reaction of interest to automotive exhaust gas catalysis. The selectivity of a reaction is defined as the ratio of conversion to desired products *versus* total conversion. The important overall reactions are given in equations (1) and (2).



Reaction (1) is desirable and reaction (2) has to be suppressed. For both reactions NO has to dissociate. It appears that platinum and rhodium [7] show a completely different selectivity with respect to these two reactions. On platinum a significant amount of NH₃ is formed, whereas on rhodium the selectivity to N₂ is larger.

On a rhodium surface NO dissociates much easier than on platinum. As a result at steady rate Rh has a high coverage of adsorbed nitrogen atoms, whereas on the much less reactive platinum, the steady state coverage of N_{ads} is low. Hydrogen, though dissociating easily on every transition metal surface, has little chance to recombine with nitrogen, because of the high nitrogen coverage on the Rh surface. On Pt, however, due to its low N coverage, many sites are available, resulting in a high hydrogen coverage on this metal. Together these effects result in an enhancement of reaction (1) and suppression of reaction (2) on the surface of rhodium.

In summary, two phenomena are of importance to the selectivity of a reaction:

- *Mechanism*, which controls which molecules dissociate and also which surface intermediates recombine and which do not;
- *Surface composition*, which influences the recombination probabilities.

In our example, the rate of NH_3 production is high when the nitrogen surface coverage is low. A high nitrogen coverage corresponds to a high N_2 versus NH_3 production ratio.

The classical picture of catalysis by a surface has been provided by Langmuir [8]. He proposed a surface with a finite number of equal vacant sites. Adsorbates were supposed not to interact. Surface scientific investigations and especially STM studies have convincingly demonstrated that the reality of the reactive surface is significantly more complex [9]. Generally the interaction between adsorbates cannot be ignored. Lateral interactions may lead to non-ideal mixing behaviour of adsorbate layers. Surface adsorbate layers appear often to form ordered structures that develop into overlayer islands. Also atoms or molecules adsorbed near to each other may develop strong repulsive interactions that have to be overcome when a reaction occurs.

As we will discuss more extensively later, the interaction energy of an adatom with a surface is a strong function of the surface structure. Two geometric parameters are important:

- The number of surface substrate atoms that coordinate to the atom: the *coordination number of the adatom*;
- The degree of coordinative unsaturation of the surface substrate atoms: the *coordination number of the surface atoms with substrate neighbour atoms*.

Generally the reactivity of a surface atom decreases with decreasing coordinative unsaturation. For example, for the dense surfaces of a face centred cubic crystal, a surface atom with 9 surface atom neighbours ((111) surface) will be less reactive than one with 8 neighbours ((100) surface). It is in essence due to the law of Bond Order Conservation [4, 10] which states that

bonds become weaker the more the valence electrons have to be shared. The interaction energy of an adsorption complex is determined by the embedding of the surface complex. The lower reactivity of the surface atoms compared to those in an organometallic complex tends to lead to weaker interactions in the surface complex [13].

The increased interaction of an adsorbate atom when the coordination of surface atoms with neighbouring surface atoms decreases can provide the driving force for surface rearrangements with important consequences for catalysis. An example is the oxidation of CO on the (110) surface of platinum [11]. As is shown in Figure 3 in ultra high vacuum the Pt (110) surface reconstructs to a less reactive structure, indicated with surface-crystallographic notations Pt(110)-(1x2), in which a row of atoms is missing. Coordinatively unsaturated atoms contract their surface bonds, thus generating surface stress forces. The driving force for the reconstruction is surface stress relief.

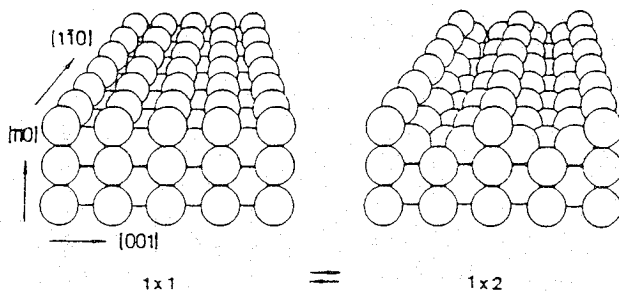


Figure 3. The (110) surface of platinum (left) and its (1x2) reconstruction (right)

As a consequence, a less reactive surface is formed. During reaction the surface alternates between the nonreconstructed and reconstructed phase. Surface conversions to the non-reconstructed phase is driven by the lower degree of coordination of the surface atoms and hence a higher reactivity. Surface reconstruction may also lead to more favourable coordination of the adatom itself.

At low surface coverage an adsorbed atom will usually not disrupt the surface lattice, but pull surface atoms outwards from the surface to form a surface complex embedded in the metal surface [12]. Adsorbates tend to form chemisorbed complexes that are structurally close to the analogous coordination complex. The local surface structural change is counteracted by surface stress forces that respond to the local surface strain of the adsorption site. When more atoms adsorb, surface stress can be released by rearrangement of surface atoms [14], as we discussed earlier for the reconstructed Pt (110) surface. The reconstructed surface will create sites that have stronger

interaction with the adsorbate. This may lead to the formation of ordered overlayers with transport of surface atoms. Facetting of surfaces to give surface phases stable during reaction may occur after an initial period.

The chemical reactivity of adsorbed atoms may also change as a function of surface concentration and composition. For adsorbed oxygen Roberts [15] has proposed a difference between the reactivity of isolated oxygen atoms and oxygen atoms that are part of an oxygen overlayer structure. Isolated oxygen atoms adsorbed to a Cu (111) surface have been found to be highly reactive and to promote dissociative adsorption of NH_3 . However, oxygen atoms that are part of an oxidic overlayer are found to be non-reactive. This may be due to the extra stabilisation of oxygen atoms in reconstructed overlayers. It is illustrated by an interesting reactivity study of Bowker [16] of the reactivity of adsorbed methoxy species with an overlayer of adsorbed oxygen on a reconstructed Cu (110) surface. Using STM it was found that only atoms on edges into the direction of an oxygen overlayer would be activated by interaction with the methoxy CH bonds (Figure 4).

The presence of lateral interactions between atoms adsorbed in the surface layer can also have an important consequence for the selectivity of a reaction. For instance, the selectivity of the epoxidation reaction of ethylene by oxygen appears to be strongly dependent on the composition of the surface oxygen layer present on the silver catalyst [7]

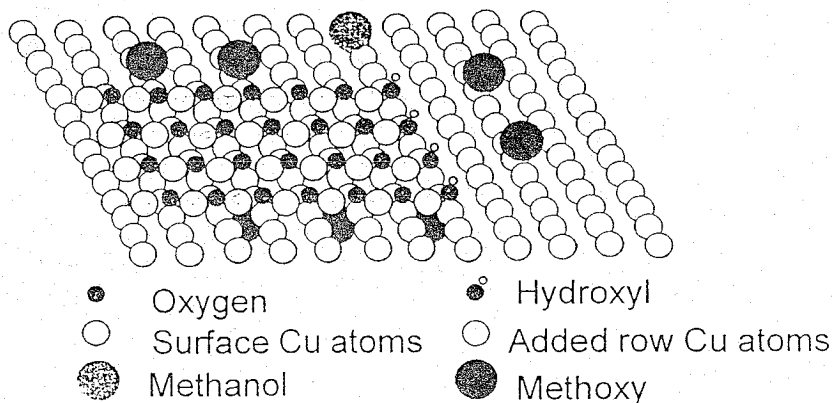


Figure 4. Reactivity of methoxy species on Cu (119) (reference 16)

At high oxygen surface coverage selective conversion of ethylene to epoxide occurs. The surface layer then has a stoichiometric composition of AgO , with part of the oxygen atoms located in a subsurface layer and other oxygen atoms adsorbed in the external surface layer. The nature of adsorbed oxygen atoms

has become electrophilic and favourable for insertion into the π bond of ethylene.

The microscopic picture of catalysis that evolves is a dynamic one. The timescale of a catalytic event is typically a millisecond or larger. However, surface atoms will locally rearrange on a picosecond timescale, the same timescale at which adsorbate molecules will equilibrate to the surface. On a microsecond timescale, surface diffusion and surface reaction events can take place as illustrated in Figure 5.

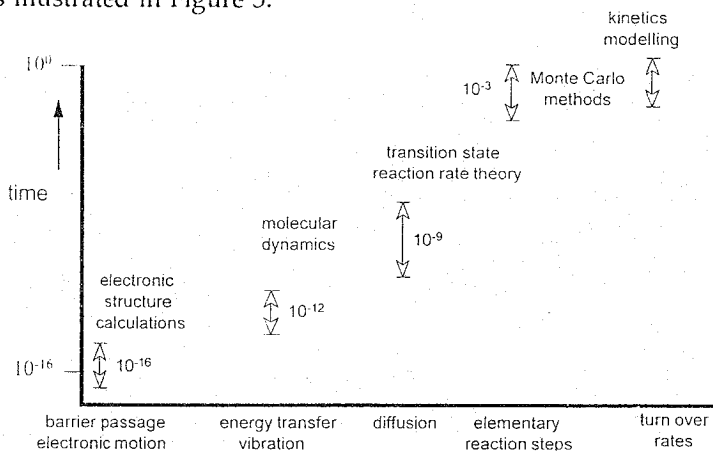


Figure 5. Time scales in catalysis

This leads to a hierarchy of events. Parameters deduced from short time scale processes can be used in the equations corresponding to the slower processes. This provides a means to bridge the molecular and macroscopic sciences gap (see Figure 6). The kinetic equations contain rate parameters (equilibrium constants, activation energies, pre-exponents) that can, in principle, be deduced from molecular theory [5]. In the next paragraph we will describe essential features of the four main elementary steps that contribute to the catalytic reaction cycle.

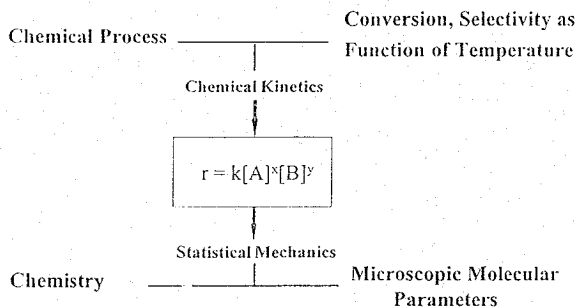


Figure 6. Hierarchy of events

2. Chemisorption

Whereas the bond strength of atoms such as O or C to a transition metal surface typically are of the order of 500 kJ/mol, the interaction energy between an adsorbed molecule and a transition metal surface is much weaker. It may typically vary between 50 kJ/mol as for NH₃ on Cu and 160 kJ/mol as for CO on cobalt. The much stronger bonding of adatoms can be readily understood. In a molecule, the valence electrons are saturated by molecular bonds, whereas the valence electrons of an atom are freely available. The asymmetric 2p_x and 2p_y atomic orbitals of C and O (the z axis is chosen perpendicular to the surface) require asymmetric surface orbitals for bonding. On a surface asymmetric orbitals can be d-orbitals centred on the atoms or asymmetric linear combinations of s-atomic orbitals (surface group orbitals [4]) between atoms.

As is also illustrated in Figure 7, symmetric p_z orbitals can only overlap with symmetric surface group orbitals. In contrast to the 2p_x and 2p_y atomic orbitals, the p_z orbital has also a finite overlap with an s-atomic orbital when adsorbed on top of an atom.

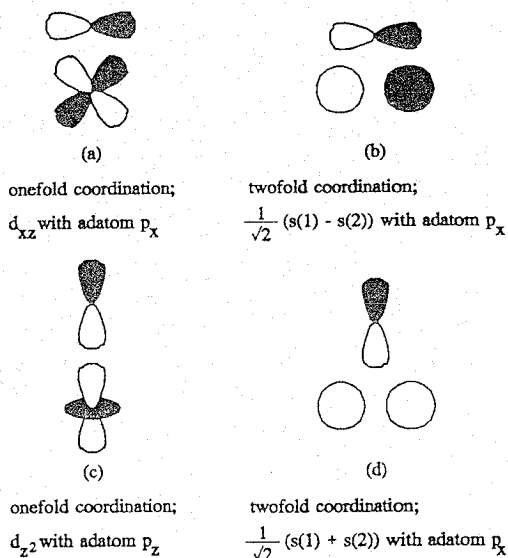


Figure 7. Symmetry combinations of surface orbitals

On most of the transition metal surfaces the overlap between adatom valence electrons and metal s-valence electrons (occupied by approximately one electron per atom, the contribution of p-atomic orbitals is usually small) dominates the bond energy. This favours high coordination (twofold or

higher) for adatoms, otherwise the asymmetric atomic p_x and p_y orbitals could not contribute to the chemical surface bond.

The interaction with the metal d -valence electrons (see Figure 8) gives a small but significant contribution to the interaction energy. It determines largely the differences in bonding to different metals because of the variation in the total number of d -valence electrons and d -atomic orbital spatial extension. This will be illustrated for the interaction of the CO valence electrons with the d -valence electrons of a transition metal. The HOMO (Highest Occupied Molecular Orbital) of CO is a 5σ orbital. When CO is chemisorbed to a surface, the 5σ orbital is directed towards the surface and can only overlap with symmetric surface orbitals. CO has two LUMOs (Lowest Unoccupied Molecular Orbital), The $2\pi^*$ orbitals that in the adsorbed state are asymmetric with respect to the surface normal. The resulting orbital interaction scheme is sketched in Figure 9. Bonding as well as anti-bonding orbital combinations are formed.

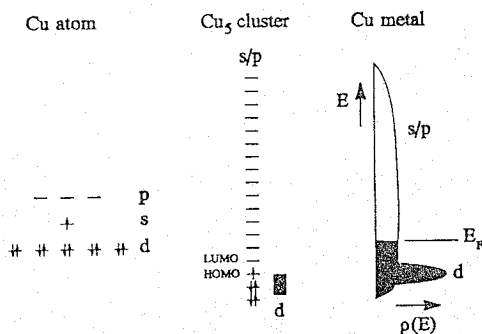


Figure 8. Schematic representation of the s -, p -, and d -orbitals on a copper atom, cluster and metal

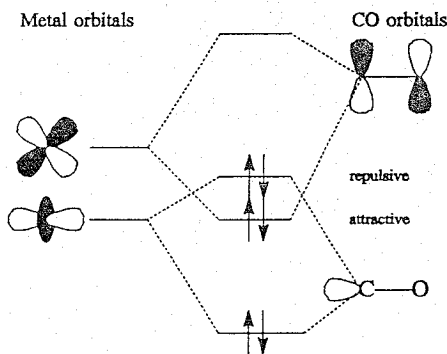


Figure 9. Interaction of CO HOMO (5σ) and LUMO ($2\pi^*$) with copper orbitals $3d_{z^2}$ and $3d_{xy/yz}$

Whereas the metal electrons will mainly occupy bonding orbital fragments between the adsorbate LUMO ($2\pi^*$) and surface orbitals (the energy position of the anti-bonding fragments is too high), in the case of interaction with the adsorbate LUMO orbital, antibonding orbital fragments will become occupied to a significant extent [4].

Whereas electron occupation of bonding orbitals strengthens a bond and because of the larger orbital overlap, will favour bonding to high coordination sites, electron occupation of anti-bonding orbital fragments will weaken the chemical bond. It leads to repulsive interactions that are minimised when bond overlap is least, *i.e.* in low coordination sites. The larger the number of *d*-valence electrons, the more anti-bonding surface orbital fragments become occupied and the weaker the surface bond becomes. Whereas for adatoms, dominated by the interaction with the adatom $2p$ orbitals this results in significant changes in the bond energy, these changes may be much less for adsorbed molecules. With an increase in the number of surface *d*-valence electrons the increase in the occupation of the bonding surface-LUMO ($2\pi^*$) orbitals, which are attractive, will partially off-set the repulsive increase in the occupation of the anti-bonding surface-HOMO (5σ) orbitals.

Also the differences in energy for molecules adsorbed one-fold, two-fold or higher are small and often molecular adsorption to one-fold coordination is found to be preferred.

A similar feature is found when one compares the bond energies of adatoms between different surfaces of the same metal. Because of the decrease in delocalisation of the metal valence electrons when their coordination number decreases, the overlap with adsorbate orbitals increases. This again enhances bonding interactions. However, it destabilises the anti-bonding orbitals. The overall effect is an increase in the interaction energy with adsorbates, but less for molecules than for atoms.

Of importance for our next subject, dissociation, is also the weakening of intramolecular bonds by adsorption. The occupation of valence electrons of orbital fragments that are formed between the metal valence band and unoccupied adsorbed $2\pi^*$ orbitals, implies that in the chemisorbed state the CO $2\pi^*$ orbitals become occupied. Electron population of these anti-bonding orbitals give a weakening of these bonds, experimentally observed by a decrease in the CO bond frequencies.

The balance between the interaction of HOMO and LUMO adsorbate orbitals with surface orbitals may vary largely between adsorbates. For adsorbed ammonia molecules the interaction with the HOMO dominates. In molecules as NO and O₂ the interaction with LUMOs is strong and more enhanced than in CO, because of their lower energies.

The rate of molecular adsorption is usually large. The sticking coefficient, the ratio between the number of collisions that lead to adsorption and the total number of collisions varies between 0.1 and 1. Molecular adsorption is usually unactivated and determined by the rate of energy exchange between adsorbing molecule and the surface.

The rate of desorption is slow compared to adsorption because the heat of adsorption has to be overcome. The activation energy for desorption is often close to the heat of adsorption. The pre-exponent for desorption is often high $\sim 10^{16} \text{ sec}^{-1}$, because of the gain in entropy of the desorbing molecule.

3. Dissociation

3.1 THERMODYNAMICS

Figure 10 illustrates schematically the differences in the heats of adsorption of CO on surfaces of Cu, Ni and Co and the energies of the dissociation products. As expected from the previous analysis, the differences in energies between the adatoms are much larger than the differences in the molecular adsorption energies. The energies are found to decrease with d-electron valence occupation.

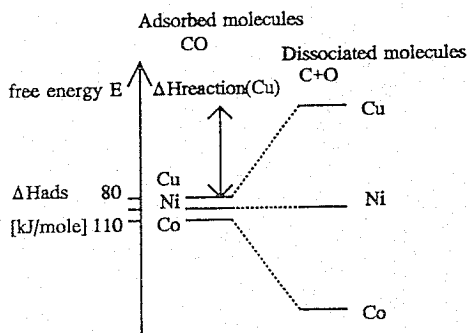


Figure 10: Reaction energy scheme for the dissociation of CO

As a consequence, CO will not dissociate on Cu; dissociation is thermodynamically neutral on Ni and exothermic on Co. For the conversion of synthesis gas (a mixture of CO and H₂), it explains the difference in selectivity between these metals. Cu is an active component of methanol synthesis catalysts. Ni is a methylation catalyst and Co is a Fischer-Tropsch catalyst that produces higher hydrocarbons. In order to produce higher hydrocarbons, C₁ intermediates are needed that are strongly bonded, so that chain growth will compete with methylation [4]. Thermodynamics also relates to large differences in the overall reaction rates, when dissociation is rate-limiting. An example is provided by the data of Somorjai [18] (Figure

11). He studied the reaction of N_2 with H_2 to produce NH_3 and found that surfaces with reactive surface atoms (low surface coordination) are most active. On such a surface the rate of dissociation is highest. The relation between the thermodynamics of a reaction and the rate of a reaction is given by the Brønsted–Polanyi relation. According to this relation, as long as the reaction path remains similar, the change in activation energy of the reaction rate constant is proportional to the change in reaction energy:

$$\Delta E_{act} = 1/2 \Delta E_{reaction} \quad (3)$$

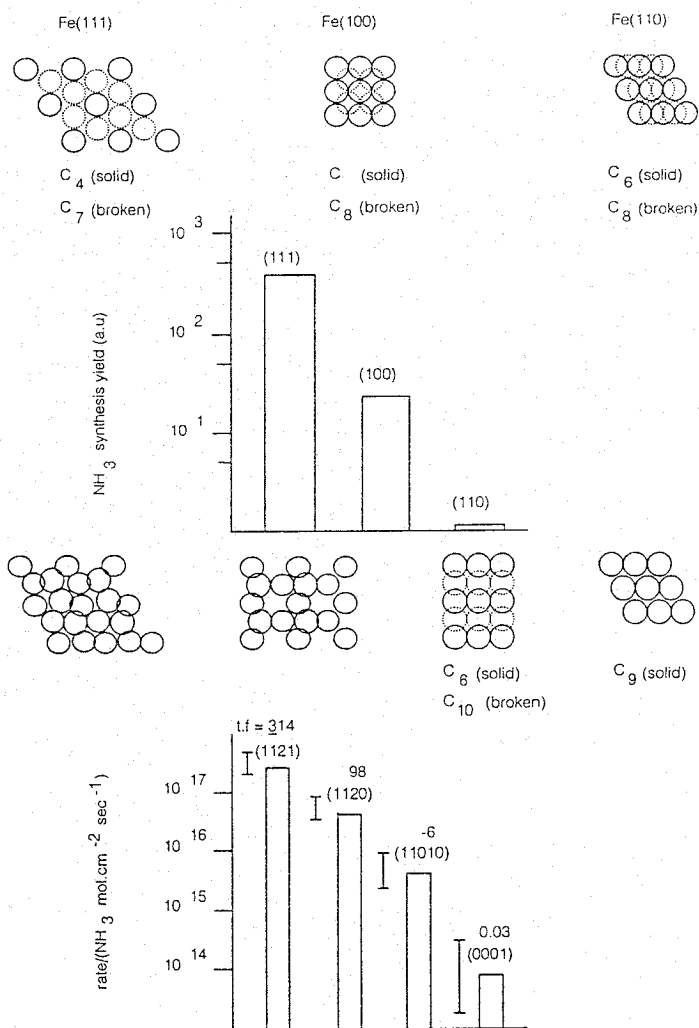


Figure 11. Reactivity of different surfaces of Fe for the formation of NH_3 from N_2 and H_2 [8]

3.2 KINETICS

3.2.1 Transition Metal Catalysis:

For CO, NO and CH₄ calculations at different levels of accuracy have provided [4] a detailed picture of paths for dissociation. The dissociation path is controlled by two factors:

- Minimisation of the Transition State Barrier
- Stabilisation of dissociation products

Figure 12 [4] illustrates this for the transition state of NO on a cluster representative of the (111) surface of Cu. In the transition state the LUMO of NO has to have optimum overlap with surface orbitals. Dissociation over the top of a surface atom provides maximum overlap with asymmetric d-atomic orbitals. The N and O atoms that are generated upon dissociation adsorb in three fold coordination sites. As a consequence for NO dissociation a surface ensemble of five surface atoms is needed. This is a very general result and is called the ensemble effect. This is a very general result and is called the ensemble effect. The ensemble effect in catalysis is very general for dissociation reactions. It has been discovered by its extreme sensitivity for site blocking, and has been widely discussed for alloy catalysis.



Figure 12. Transition state for dissociation of NO

One distinguishes the primary and secondary ensemble effects [19]: the primary ensemble effect is illustrated in Figure 13. It concerns the suppression of heptane cracking when a reactive metal surface such as Pt is alloyed with a non-reactive metal such as Au.

Chemisorption of heptane to a transition metal occurs by C-H bond cleavage and coordination of several of the molecular carbon atoms to the metal surface. A large ensemble of surface atoms is needed to accommodate such an adsorbed molecular fragment. Carbon-carbon bond cleavage to produce smaller hydrocarbon fragments occurs from such a multiple bonded state. Alloying with inert atoms (*e.g.* Au) but also coadsorption of S, will decrease the surface atom ensemble size and hence decrease the probability of multi atom interaction of the molecule.

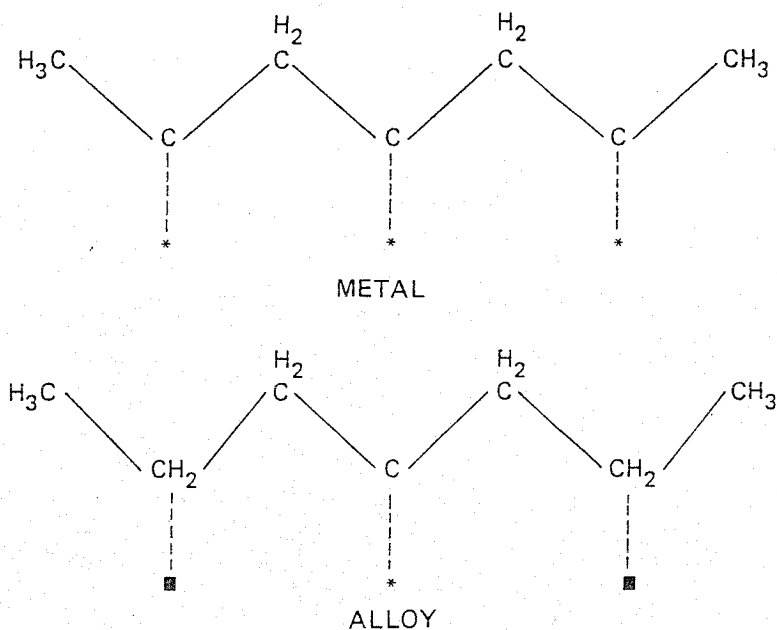


Figure 13. Primary ensemble effect

The secondary ensemble effect considers the number of surface atoms that participate in a bond with an adsorbate atom. It is illustrated in Figure 14. On a pure Pd surface, CO prefers two-fold coordination to surface Pd atoms. The bond energy of CO with the Pd surface is weakened when Pd is alloyed with Au. Alloying of Au with Pd decreases the ensemble size of the Pd surface sites. It forces the CO molecule to bind only to single Pd atoms. As a consequence, the bond energy of adsorbed CO weakens.

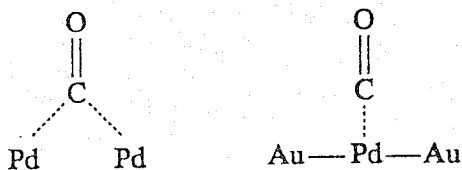


Figure 14. Secondary ensemble effect. Change in coordination of CO upon alloying of Pd with Au (schematic)

The rate constant for dissociation of adsorbed molecules sometimes has an activation energy that is close to or higher than that of desorption. This is the reason that sometimes molecules cannot be activated when in their chemisorbed state. The rate of desorption then is fast compared to that of

dissociation. In contrast to the pre-exponent for the rate of desorption, the exponent for the rate of surface dissociation is usually low $\sim 10^{13} \text{ sec}^{-1}$, because of the tight nature of the transition state [4].

The overall rate for dissociation is extremely coverage dependent because of the need for a surface ensemble. A typical form for the overall rate equation of dissociation, r_{diss} is:

$$r_{diss} = k_{diss}\theta(1-\theta)^x, \quad (4a)$$

where k_{diss} is the rate constant for dissociation of the adsorbed molecule, θ the surface coverage, x depends on the ensemble size requirement. Substituting the Langmuir expression for the coverage θ gives:

$$r_{diss} = k_{diss} \frac{K_{eq} \cdot P}{(1 + K_{eq} \cdot \beta)^{x+1}} \quad (4b)$$

where K_{eq} is the molecular adsorption equilibrium constant, p is its pressure. One notes that as predicted by Sabatier, expression (4a) has a maximum for a particular coverage (e.g. $x = 1$, $\theta_{max} = 1/2$).

From expression (4a) it follows that at low coverage the apparent activation energy of the reaction is:

$$E_{app} = E_{act}(diss) - E_{ads} \quad (\theta \ll 1) \quad (5a)$$

At high coverage, one finds:

$$E_{app} = E_{act}(diss) + xE_{ads} \quad (\theta \approx 1) \quad (5b)$$

To obtain the apparent activation energy at low coverage, one has to subtract the heat of adsorption from the surface activation energy for dissociation; at high coverage it has to be added. It reflects the need to remove adsorbed molecules in order to create surface vacancies for the dissociating molecule. Desorption will cause a decrease in the apparent activation energy with temperature.

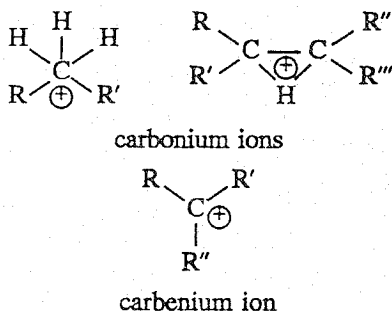


Figure 15. Carbonium and carbenium ions

A consequence of the coverage dependent apparent activation energy is that it will depend on temperature. The apparent activation energy will decrease with increasing temperature. Interestingly, according to (2), an increase in catalytic reactivity can have several reasons. An increase in heat of adsorption enhances the rate at low coverages, or a decrease in the heat of adsorption will increase the overall rate at high coverage. We recognise the principle of Sabatier. Alternatively, the intrinsic rate of the elementary surface reaction step can increase. It is becoming apparent in metal as well as zeolite catalysis that often the adsorption effect dominates.

3.2.2 Transition States in Proton Transfer Reactions

Whereas on a transition metal surface a low activation barrier for reaction is due to the large overlap between adsorbate and surface orbitals, activation of acid catalysed reactions is quite different. Reactions that are activated by proton addition proceed *via* intermediate carbonium ion or carbenium ion formation. For a carbonium ion a proton has been added to a saturated hydrocarbon. A carbenium ion is planar three coordinated positively charged ion (Figure 15), that can be generated by proton addition to an olefin. Such ions have been observed in mass spectrometers. Computational chemistry has recently significantly elucidated the nature of these intermediates in solid acid catalysis [20]. We will illustrate this for the protonation reaction of an olefin [21] and cracking and dehydrogenation [22] of ethane by zeolitic protons. Protonation of an olefin initiates many acid catalysed reactions as oligomerisation or isomerisation reactions. The initial transition and final state of the protonation reaction of ethylene are sketched in Figure 16. Initially ethylene adsorbs π bonded to the proton. Proton transfer to the molecule implies separation of charge. Due to the strong zeolitic OH bond, an energy barrier has to be overcome for dissociation of the proton. The negative charge around the alumino-ion generated by proton-abstraction, becomes redistributed on the surrounding oxygen atoms. The energy cost for proton transfer becomes minimised when the positive charge that develops on the protonated ethylene can become compensated by the negative charge of the basic oxygen atoms around aluminium. The resulting carbenium-ion like intermediate appears to be a transition state on the potential energy maximum of a reaction path that leads to an adsorbed σ -bonded ethoxy intermediate. Consecutive reactions may occur from the ethoxy intermediates.

The transformation of carbonium ions into carbenium ions is seen in the two reactions of ethane (Figure 17). Reaction of the proton with ethane can result in different reaction paths. In one reaction path the C-C bond breaks, methane desorbs and a surface methoxy species is formed (Figure 17a). In another reaction path ethane is dehydrogenated, a CH bond breaks and a surface ethoxy species is formed (Figure 17b).

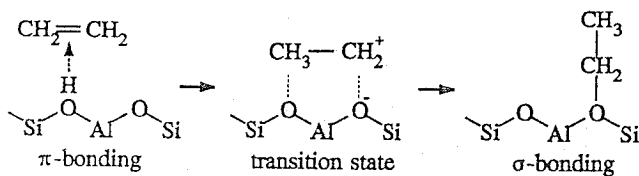


Figure 16. Protonation of ethylene; π - and σ -bonded ethylene [21]

Again the protonated intermediate species are transition states. In the transition state of the ethane cracking reaction, a carbenium type CH_3^+ is formed, that adsorbs to zeolitic oxygen to form the adsorbed methoxy species. The carbonium ion transition state for ethane dehydrogenation (barrier high ≈ 290 kJ/mole) is very different from that of cracking. It resembles a carbenium ion with weakly bonded H_2 . The carbenium intermediate adsorbs to a basic oxygen atom in the product state to form ethoxylate.

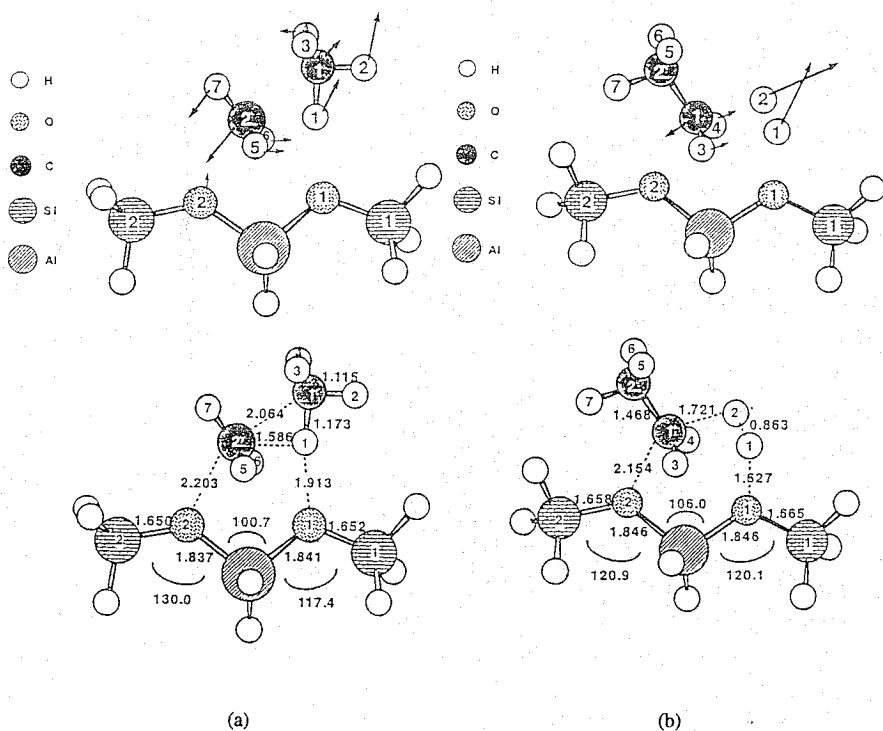


Figure 17. Transition states for ethane cracking (a) and ethane dehydrogenation (b) [22]

The Zwitter-ionic reaction paths are seen to involve several oxygen atoms around an Al site. Electrostatic stabilisation is kept optimum by the closeness

of positive charge in the transition state molecule and negative charge of the lattice. The protonation reaction can be considered a Lewis base–Brønsted acid catalytic reaction.

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