Catalysis Lectures
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Handouts: Norskov et al., J. Catalysis
        Imbihl and Ertl, Chem. Rev. (partial)
        Homework

Major points:

1) Why reactions have barriers, and how catalysts avoid/reduce these barriers.
2) Why thermochemistry of the catalyst-substrate complex is so important.
3) Homogeneous Catalysts and Heterogeneous Catalysts are NOT hugely different.
4) How Homogeneous and Heterogeneous Catalysts are different
5) Chain-Reaction Kinetics in General
6) Some important types of catalysis
    a. Dissociative Chemisorption (see Norskov et al. J. Catalysis)
    b. Protons
    c. Lewis Acids (vacant orbitals)
    d. Free Radicals
7) Langmuir-Hinshelwood vs. Eley-Rideal
8) Catalyst oscillations / microscopic dynamics

WHY REACTIONS HAVE BARRIERS
Usually, reactions have barriers because:
    a) closed shell orbitals repel
    b) steric strains to reach TS
    c) most reactions except ion-molecule and radical recombination have some barrier since molecule has to rearrange to reach TS.

Many catalysts have a vacant orbital that can accept an electron or electron pair, dramatically lowering barriers, completely changing reaction path: Transition Metals, Lewis acids, Free Radicals. Many catalysts are charged: acids, bases, metal ions, oxides.

Some catalysts provide a path that avoids steric strain, e.g. H2O can pass protons around.

A few catalysts are less dramatic: they don't change the reaction path much, but instead have some weak interactions which stabilize the TS more than the reactants. Each H-bond is worth 5 kcal/mol; enough van der Waals contacts can add up.

THERMOCHEMISTRY IS KEY
We are going from catalyst + reactants to catalyst + products, with a fixed free energy difference. We want to avoid any steps with free energy differences much larger than this – they will introduce effective activation energies (even if there is no kinetic barrier beyond the intermediate's thermochemsitry. Best if the intermediates are all intermediate in energy between reactants+catalyst and products+catalyst.

Examples:
H_3O^+ + enol = intermediate = H_3O^+ + ketone   Intermediate higher in energy than reactant so there must be a barrier just from thermo.

H + enol = intermediate = H + ketone   I think intermediate lower in energy than reactant, no barrier caused by thermo. (Will be small kinetic barrier to H addition to double bond).

In this case, Lewis acids probably won't work, since they will complex with O or double bond. But they work well for hydrocarbon isomerization (by pulling off hydride, making carbenium ion with vacant orbital).

Bases can pull proton off ketone, but also will likely react by other channels in competition.

The first thing to do when analyzing a proposed catalytic cycle is draw a PES with the intermediates, to see what is the highest energy intermediate, and whether this species is introducing a significant thermodynamic barrier.

Another critical aspect of thermochemistry is the strength of the catalyst-substrate binding. If the binding is too weak, rates will be low because not enough catalyst-substrate complex – not effectively using the catalyst, and most of the substrate is reacting some other way rather than through the desired catalytic route. If binding is too strong, kinetics will be controlled by difficulty getting substrate off the binding site. So for example there are several metals known which react with N2 to make nitrides, but most of

these are useless as catalysts for making NH3 because it takes too much energy to get the N off the catalyst.

Barriers usually highly correlated with thermo: exothermic reactions have low barriers. So you can usually accelerate a process by making the rate-limiting step more exothermic.

If you vary the thermochemistry of an intermediate, you usually see a VOLCANO PLOT.

Just because a catalyst-substrate complex is stable doesn't mean it is important in the reaction. Could just be a dead-end – very often the major species observed in surface science are irrelevant.

HOMOGENEOUS CATALYSTS vs. HETEROGENEOUS CATALYSTS
In most cases, there are homogeneous catalysts that can do exactly the same thing as a heterogeneous catalyst, with a comparable rate. Many heterogeneous catalysts are just a tethered version of a homogeneous catalyst. At the microscopic, bond-breaking, bond-making level, usually only a few atoms close to the bond being broken/formed are critical.
Big practical difference is that it is easy to separate/immobilize heterogeneous catalyst. Also, heterogeneous catalysts have some diffusion limitations that don't afflict homogeneous catalysts. And heterogeneous catalysts are almost always heterogeneous: many different sites, surface structure unknown, very difficult to work out what is really important.
A few heterogeneous and homogeneous catalysts are shape-selective, e.g. enzymes, single-site catalysts, chiral catalysts, zeolites. But most catalysts are not shape-selective.
Metals are really different than homogeneous catalysts:
    Different active sites affect each other strongly
    Electronic bands rather than electronic states
    Long-range image-charge interactions
    Often substrates have very high mobility on metal surfaces.
But many metal-containing catalysts are not conductors, just salts, work fine without all this fancy collective interaction stuff.

CHAIN REACTION KINETICS

Usually, there is a main chain reaction and some possible side chain reactions. And on a much slower timescale there are processes which change the amount of catalyst.

Note that in a catalytic cycle / chain reaction at steady-state all the steps have exactly the same net rate; the concentrations of the intermediates adjusts so that there are a lot of reactants for the slow step, and only a few for the fast-step(s). One speaks of the chain-carrying radical, or of the dominant surface intermediate. (Note that there can be radicals which are not part of the chain, and surface species which are not intermediates in the desired reaction.)

For free radical catalysis, the catalysts are very unstable and must be continually generated (somehow). In aqueous solution, protons and hydroxide ions are continually generated and destroyed. For metals, there are usually "poison" ligands which reduce the catalytic activity; when you synthesize a metal-containing catalyst there is usually a critical step when you 'activate' the catalyst by destroying/driving off the poisons on its surface. Poisons are often made as byproducts of the reaction; catalysts often also sinter or dissolve into the bulk support material.

TON = number of products formed per second / number of active catalysts
Chain length = TON * avg. catalyst lifetime = # products formed / catalyst formed

Instantaneously, the slow processes are not important. But over the long haul they are critical.

SOME IMPORTANT TYPES OF CATALYSIS

Dissociative Chemisorption (Norskov article)
        Many important cases where a gas-phase species fragments upon chemisorption onto a metal: O_2, CO, NO, H_2, N_2, sometimes R-H. In these cases, the chemisorption step can be rate-limiting. Or if the chemisorbed species are bound too strongly they may block the surface sites so the second species they are supposed to react with can't get on to the surface. Norskov has found a universal Evans-Polanyi relation between Ea for dissociative chemisorption and the chemisorption thermochemistry. For the chemisorbed species to bind to most of the sites but still leave some sites open, you want
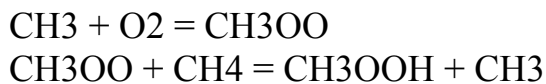
delta H binding ~ 1 eV ~ 25 kcal/mole (in this case deltaG ~ 0 at 1 atm because of big T delta S between chemisorbed and gas-phase species.) Norskov finds that you can explain which metals work for which diatomics just from this chemisorbtion thermo, and then showed that you can understand why some alloys work (because they have the right thermo).
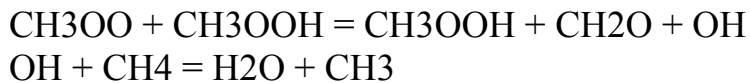
FREE RADICAL REACTIONS
The radicals are the catalysts for the main (propagation) cycle. If you can maintain a higher steady-state radical concentration, or convert the least reactive 'chain-carrying' radical into something more active you could accelerate the chain reaction (or even change its products).

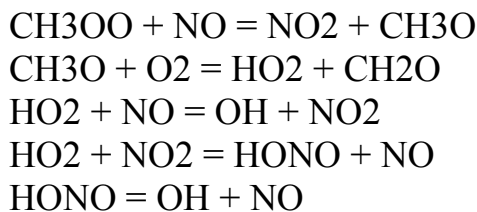One Example: Methane oxidation catalyzed by NOx

Without NOx:

$$CH3 + O2 = CH3OO$$
$$CH3OO + CH4 = CH3OOH + CH3$$

But CH3OOH is more reactive than CH4, so

$$CH3OO + CH3OOH = CH3OOH + CH2O + OH$$
$$OH + CH4 = H2O + CH3$$

But CH2O more reactive than either

$$CH3OO + CH2O = CH3OOH + HCO$$
$$HCO + O2 = HO2 + CO$$
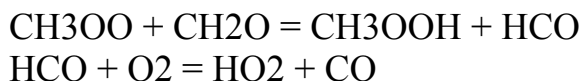
Takes reaction too far, all the way to CO!

With NOx:

$$CH3OO + NO = NO2 + CH3O$$
$$CH3O + O2 = HO2 + CH2O$$
$$HO2 + NO = OH + NO2$$
$$HO2 + NO2 = HONO + NO$$
$$HONO = OH + NO$$

So NOx converts CH3OO and HOO into OH, much less selective i.e. more likely to attack CH4 than CH2O

Another example: Fenton Chemistry

Aqueous hydrogen peroxide H2O2 (in the presence of O2, either from the atmosphere or from the H2O2 decomposition) is widely used to oxidize organics around room temperature. However, the rate of the reaction is pretty slow. Here is the propagating chain:

R. + O2 = ROO.
ROO. + H2O2 = ROOH + HOO.
HOO. + RH = H2O2 + R.
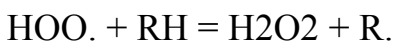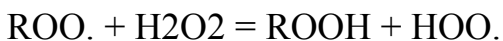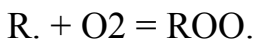
The main problem is that the steady-state radical concentration is very low. In particular the radical formation rate:

H2O2 = 2 OH
2 OH + 2 RH = 2 H2O + 2 R.
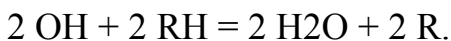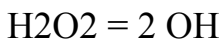
is very slow mostly because the first reaction is quite endothermic (>40 kcal/mol), and also because the chain-carrying HOO radical disproportionates more quickly than most peroxyl radicals:

2 HOO = H2O2 + O2

(Though in water, some of the HOO will be hydrogen bonded to the solvent, and some will be ionized and exist as superoxide ions; both effects reduce the disproportionation rate.)

The H2O2 dissociation to form radicals is catalyzed by metal salts, e.g. iron:

Fe(II) + H2O2 = Fe(III)OH + .OH
Fe(III)OH + H2O2 = Fe(II) + H2O + HOO.
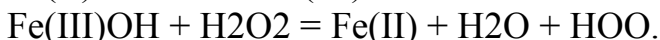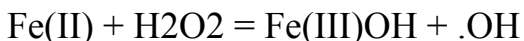
The first step is fast, the second step is rate determining. In some situations, e.g. to drive a free-radical polymerization, one wants a very high concentration of radicals, in that case one can add a reducing agent to bring the Fe(III) back to the active Fe(II) form. Some popular reducing agents used in industry are sugars.