

## ***Homogeneous vs Heterogeneous Catalysts***

| <b>Homogeneous</b>                        | <b>Heterogeneous</b>                  |
|---|---------------------------------------|
| Liquid phase                              | Liquid/gas/solid phase                |
| <b>Low temperature</b>                    | High temperature                      |
| <b>High selectivity</b>                   | Low selectivity                       |
| <b>High diffusivity</b>                   | Diffusivity can be an issue           |
| <b>Easy heat transfer</b>                 | Heat transfer can be an issue         |
| Difficult catalyst separation             | <b>Easy catalyst separation</b>       |
| Expensive recycling                       | <b>Simple recycling</b>               |
| <b>Well-defined active site</b>           | Poorly defined active site            |
| <b>Easy catalyst modification</b>         | Difficult catalyst modification       |
| <b>Reaction mechanism well understood</b> | Reaction mechanisms poorly understood |

### **- Phase**

*Homogeneous:* Liquid. When a reactant is in the gas form such as in hydrogenation, what reacts is actually the gas dissolved in the liquid phase, and not the one in the gas phase.

*Heterogeneous:* Liquid, Gas, Solid

### **- Operative Temperature**

*Homogeneous:* Generally low temperatures. The presence of a solvent, which needs to dissolve the catalyst, might limit the temperature of the reaction, but on the other hand, it forces to use mild conditions. An exception is when high pressures are used. (Why? Think about it) In such cases, what limits the reaction temperature is the stability of the homogeneous catalyst, which is known to be fairly limited.

*Heterogeneous:* The only limitation is the stability of the catalyst under harsh conditions.

### **- Diffusivity**

*Homogeneous:* High diffusivity. Having all reactants and catalyst in one phase enhances dramatically the diffusivity under proper stirring.

*Heterogeneous:* Diffusivity might be an issue for catalysts with low surface area.

### **- Heat Transfer**

*Homogeneous:* High Heat Transfer. Having all reactants and catalyst in one phase enhances dramatically the heat transfer under proper stirring.

*Heterogeneous:* Heat Transfer might be an issue due to the different heat capacities of reactants and catalyst.

### - Catalyst Separation

*Homogeneous:* The separation of the products from the catalyst is generally expensive, the only exception being in biphasic catalysis.

*Heterogeneous:* The separation of the products from the catalyst is usually straightforward.

### - Recycling

*Homogeneous:* Recycling is expensive due to difficult treatment of the spent catalyst.

*Heterogeneous:* Recycling is usually straightforward, although the catalyst might need reactivating treatment.

### - Active site

*Homogeneous:* Usually well-defined. Catalysts are generally single atom transition metal stabilized by ligands.

*Heterogeneous:* Mainly not well-defined. When dealing with metal particles on a support, the active site might be only a few percent of the metal (usually small particles), and different zones of the same particle might have different catalytic properties.

### - Catalyst modification

*Homogeneous:* Relatively easy. Tuning of the electronic and steric properties on the metal can be done by varying donor atoms in the ligands or by tuning the donating abilities of the ligands. For example, if triphenylphosphine is the ligand and one needs to have a less donating phosphine, the phenyl groups on the phosphine could be tuned (adding CF<sub>3</sub>, F, and other electron withdrawing groups). Synthetic methods available are numerous and all based on basic concepts developed in organic and organometallic chemistry.

*Heterogeneous:* Relatively difficult. Control of the particle size and of the active site in general at the molecular level is extremely difficult. Few synthetic methods are available.

### - Reaction Mechanism

*Homogeneous:* Easier to find out due to more techniques available. Direct methods are available (they look at catalyst and not at the products of the reaction). In addition to those of heterogeneous catalysis (see below) the most common techniques are:

- Liquid state NMR: Useful in kinetics for relatively slow reactions and to identify intermediate states *of the catalyst*. Limited to diamagnetic metal complexes.
- Single crystal X-ray diffraction: Useful to identify the intermediate states *of the catalyst*.
- Computational methods are more accurate due to discrete molecular orbitals as theoretical model.

*Heterogeneous:* Difficult to find out. Mainly by indirect methods (they look at products and not at the catalyst itself). Available techniques are:

- Infrared spectroscopy: Useful to determine the species absorbed on active site. STRONGLY limited by the presence of groups that can be distinguished in the IR spectrum. Computational model might help to determine the structure of the reactive intermediates. Useful in kinetics as well.
- Liquid State NMR, GC-MS: Useful to determine the intermediates *of the organic reaction*.
- Electron microscopy: Ex-situ determination of particle-size.
- X-ray absorption: Ex-situ and in-situ determination of the surrounding of the metal. MUST be supported by computational models.

· Computational methods are less accurate due to band theory as theoretical model.

- **Selectivity**

*Homogeneous*: High. It is a consequence of the easier fine-tuning of the steric and electronic properties of the catalyst and of the easier way of finding out the reaction mechanism.

*Heterogeneous*: Low. It is a consequence of more difficult fine-tuning of the steric and electronic properties of the catalyst and of the more difficult way of finding out the reaction mechanism.