Heterogeneous catalysis (C9981)

Common Pitfalls of Catalysis Manuscripts Submitted to Chemistry of Materials

CHEMISTRY OF MATERIALS

Editorial

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Common Pitfalls of Catalysis Manuscripts Submitted to *Chemistry of Materials*

Active site/catalyst evaluation

- **Turn-over frequency** (TOF; [s^{-1}])
  = number of catalytic cycles performed by **1 active site** per time unit
- **Precise numbers for homogeneous and enzymatic catalysis**
- **Numbers for heterogeneous catalysis???**

	TOF [s^{-1}]
Hetero:	~1–100 s^{-1}
Homo:	~10–1000 s^{-1}
Enzymes:	~10000–1000000 s^{-1}

Active site/catalyst evaluation

- **Turn-over number** (TON; [-])
  = number of catalytic cycles performed by **1 active site** before deactivation (~lifetime)
- **Precise numbers for homogeneous and enzymatic catalysis**
- **Numbers for heterogeneous catalysis???**

Common pitfalls - 1

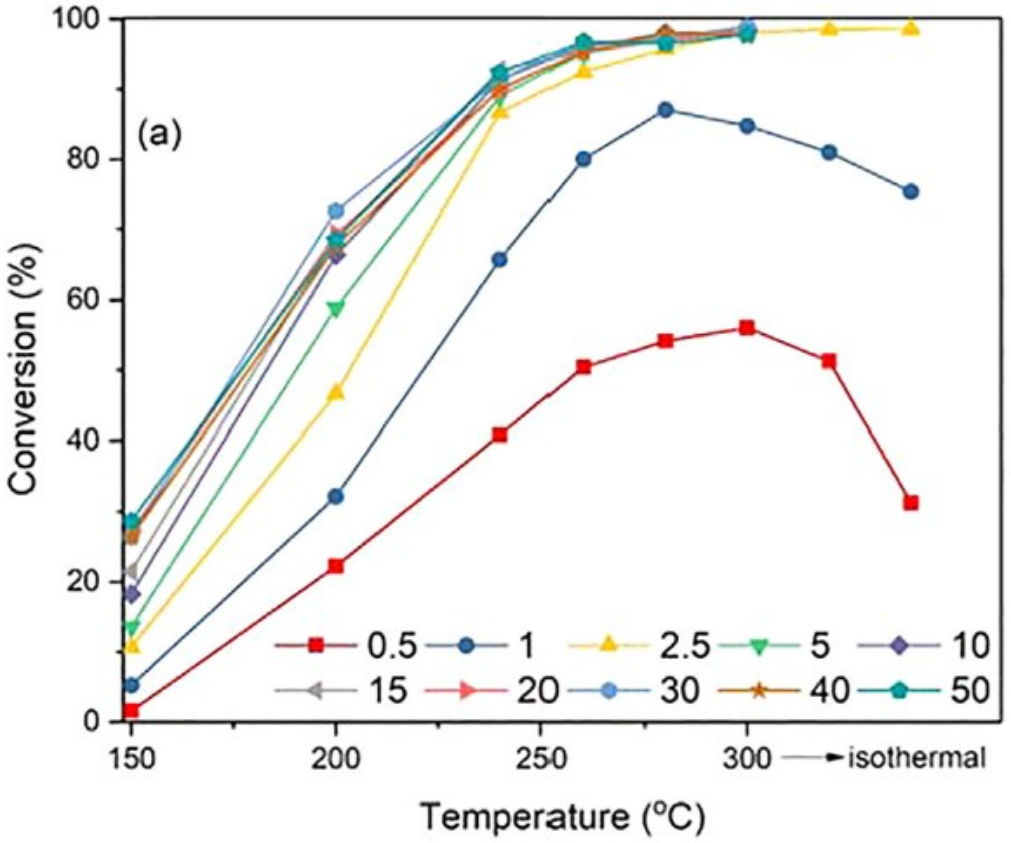
- Improper calculation of turnover frequencies (TOFs)
  - Low conversion, early stage of the rxn
  - Valid only for specific reactant concetration
- Improper calculation of turnover numbers (TONs)
  - A measure of catalyst's stability
  - Accurate determination requires measurements until the catalyst's activity is completely lost

Common pitfalls - 2

- Deactivation studies at full/equilibrium conversion
  - Batch vs. continuous flow
  - The available amount of reagents limit the conversion = the catalyst could be in fact more active
  - Deactivation should be studied at intermediate conversions

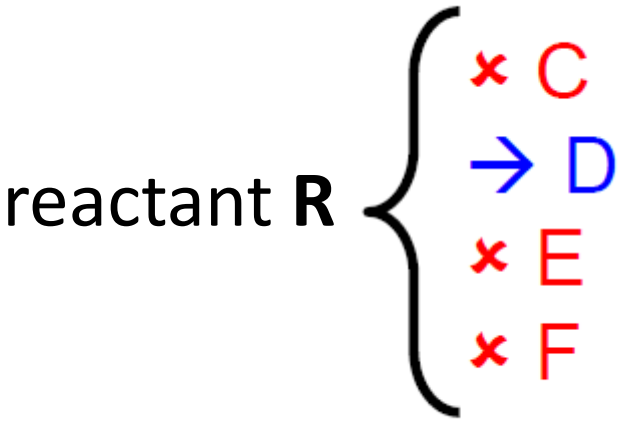
Common pitfalls - 2

- Deactivation studies at full/equilibrium conversion



Active site/catalyst evaluation

- **Selectivity** is ability of catalyst to form one product from a pool of products (possibly many)



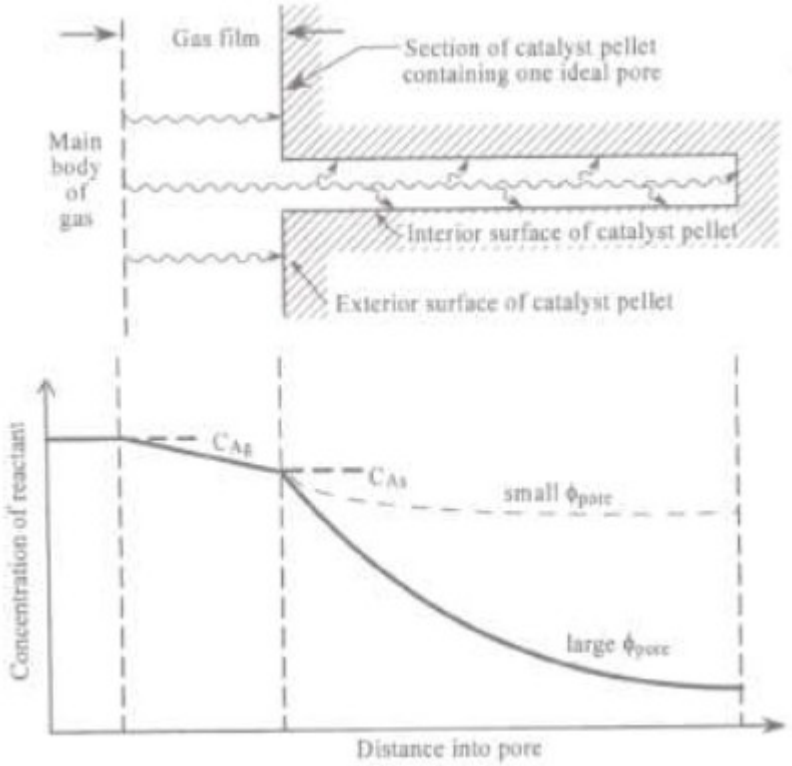
- **Selectivity** (S; [%])
  = number of D molecules produced / R molecules converted

Common pitfalls - 3

- Comparison of selectivities at different conversion levels
  - Selectivity does depend on conversion
  - A→B→C
  - Always compare at isoconversion

Diffusional limitation

- Gradient of reactant concentration in
  - Fluid film of particle (External diffusion)
  - Inside the pore (Internal diffusion)

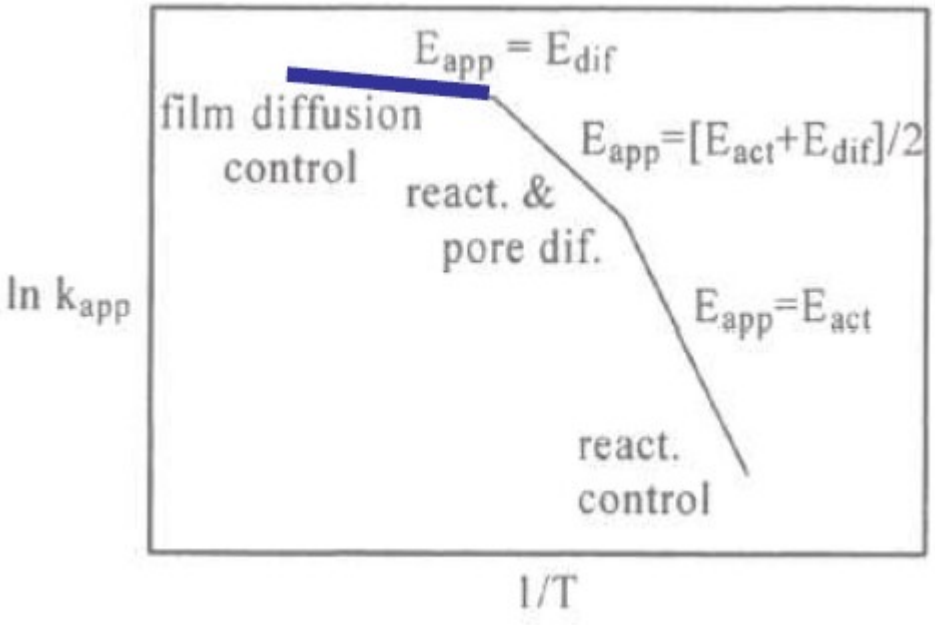


Common pitfalls - 4

- Neglect of mass transfer (diffusional) limitations
  - External (film) + Internal (pore) diffusion

Rate determining step

- High temperature
  - The chemical reaction is fast
  - There is no time for **internal diffusion** to take place, only external surface employed in catalysis
  - Diffusional steps are limiting
  - $E_{app} = E_a$ of the diffusion in the fluid film (**external diffusion**)

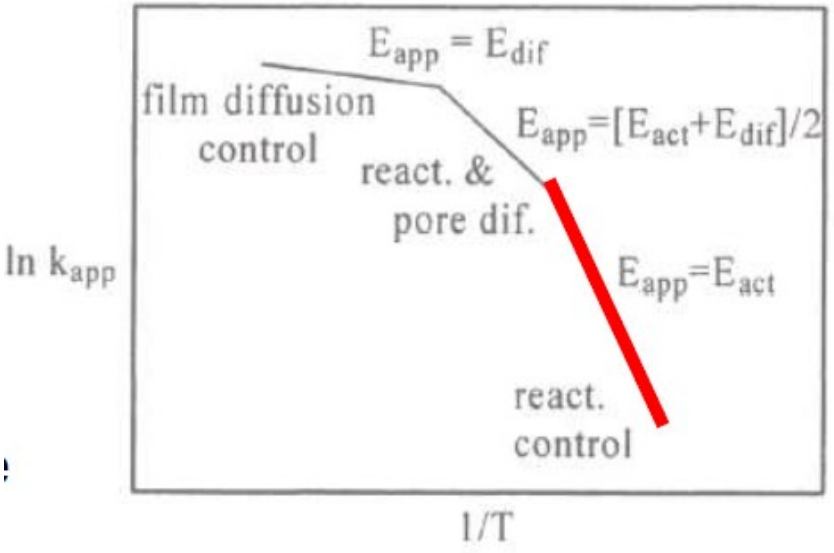


Common pitfalls - 4

- Neglect of mass transfer (diffusional) limitations
  - Batch, both diffusions: stirring rates
  - Continuous flow, external diffusion:
  - Continuous flow, internal diffusion: particle size, pore volume, pore size

Diffusional limitations

- Internal diffusional limitations always present to some extent
  - We can diminish them **at the time of catalyst preparation** (pore volume, pore diameter, size of catalysts grains)
  - Good practice is to compare a series of catalysts with similar pore volume, pore diameter, and size of catalysts grains
- External can be avoided **at the time of catalytic reaction**
  - Linear velocity of vector gas,...

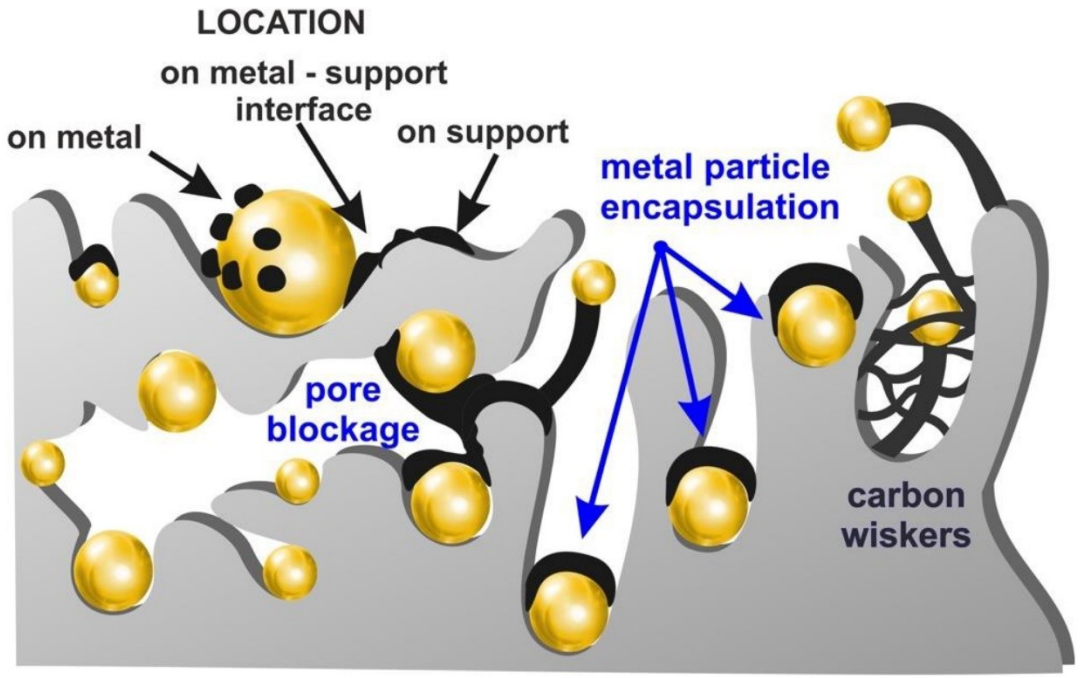


Common pitfalls - 5

- Failure to study the catalysts after reaction
  - Catalysts can change dramatically during catalytic reactions
  - Sintering, coking, pore collapse, poisoning,…
  - It is not correct to justify the differences between the catalysts only based on the characterization of the starting material

Common pitfalls - 5

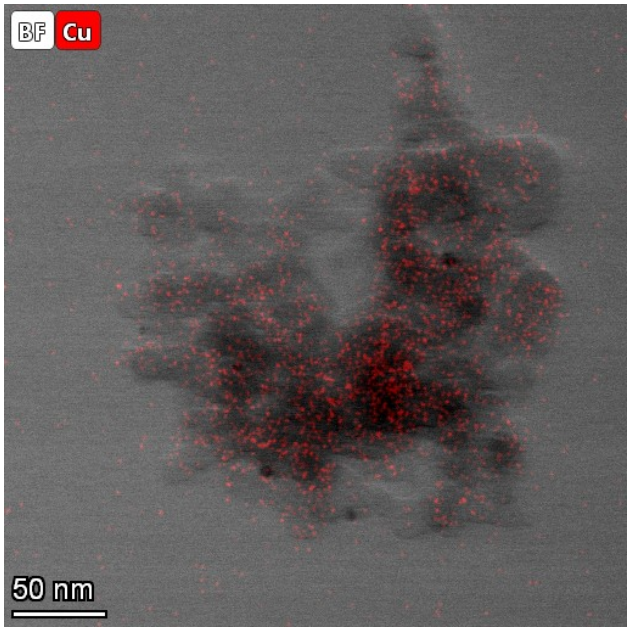
- Failure to study the catalysts after reaction
  - Catalysts can change dramatically during catalytic reactions
  - Coking



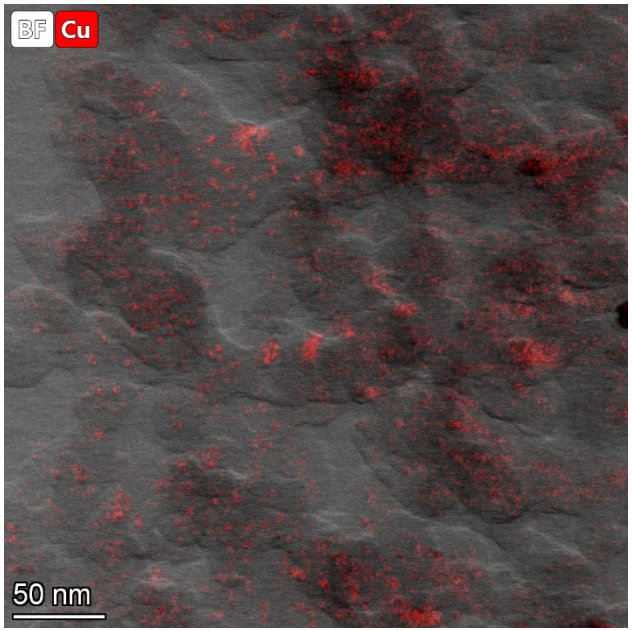
Common pitfalls - 5

- Failure to study the catalysts after reaction
  - Catalysts can change dramatically during catalytic reactions
  - Sintering

Before cata



After cata



Common pitfalls - 6

- Failure to consider differences in surface area of catalysts
  - Catalytic activity scales with number of active sites
  - Common sense: Number of active sites scales with the surface area
  - Compare the activity of catalysts per m^2