**Summary of Industrial Catalytic Processes**

|  |  |
| --- | --- |
| **Process** | **Typical Catalysts** |
| **Petroleum Refining** |  |
| **Cracking** | **Pt/Re on alumina, Zeolites** |
| **Reforming** | **Pt/Re/Ge/Sn on alumina (dehydrogenation)** |
| **Hydrocracking** | **alumina, zeolites, Pt** |
| **Alkylation** | **H2SO4, HF** |
| **Hydrodesulfurization** | **(Mo-Co) oxides, (Mo-Ni) oxides** |
| **Hydrodenitrogenation** | **(W-Ni) oxides** |
| **Chemical Manufacturing** |  |
| **Natural Gas desulfurization** | **ZnO, Cu, Fe on activated C** |
| **Hydrogenations** | **Raney Ni, Raney Co, Pt, Rh** |
| **Ammonia synthesis** | **promoted Fe** |
| **Methanol synthesis** | **Cu-ZnO** |
| **Dehydrogenation** | **Butadiene: Fe2O3, Pt/Re on alumina**  **styrene: Zn, Cr, Fe or Mn oxides** |
| **Oxidations** | **ethylene oxide: Ag**  **nitric acid: Pt/Rh mesh/gauze**  **sulfuric acid: V2O5**  **maleic, phthalic anhydrides: V2O5**  **formaldehyde: Ag or Cu; Mo, Fe, V oxides** |
| **Polymerizations** | **Ziegler-Natta polypropylene: Al alkyls + TiCl3**  **Dow single site polypropylene: Ti metallocene**  **Phillips -- Cr oxide on silica**  **Polyethylene (low density): peroxides, peresters**  **Polystyrene: benzoyl peroxide**  **Urethanes: amines, organo-tin, phosphine oxides** |
| **Hydroformylation** | **Union Carbide/Hoechst/BASF: Rh/PPh3**  **Exxon/BASF: HCo(CO)4**  **Shell: HCo(CO)4(PR3) (R = bulky alkyl)** |

**Catalytic Production of Top Organic Industrial Chemicals (old data)**

|  |  |  |
| --- | --- | --- |
| **Ranking** | **Chemical** | **Production** |
| **#4** | **Ethylene**  **33 billion lbs** | **Steam Cracking of Hydrocarbons:  larger hydrocarbon  smaller hydrocarbon + H2  C2H6(*g*)  C2H4(*g*) + H2(*g*)**  **Catalyst: Zeolites, Pt/Re on Al2O3 support  Conditions: 850°C, 20-50 atm** |
| **#10** | **Propylene**  **18 billion lbs** | **Steam Cracking of Hydrocarbons:  C3H8(*g*)  C3H6(*g*) + C2H4(*g*) + CH4(*g*) H2(*g*)**  **Catalyst: Zeolites, Pt/Re on Al2O3 support  Conditions: 850°C, 20-50 atm** |
| **#12** | **Dichloroethane**  **15 billion lbs** | ***Direct Chlorination:*  C2H4(*g*) + Cl2(*g*)  ClCH2CH2Cl(*g*) Catalyst: FeCl3 or AlCl3**  ***Oxychlorination:*  2C2H4(*g*) + 4HCl(*g*) + O2  2ClCH2CH2Cl(*g*) + 2H2O Catalyst: Cu salts on SiO2 or Al2O3 supports** |
| **#16** | **Benzene**  **10 billion lbs** | **Hydrocarbon Reforming (dehydrogenation)**  **C6H14(*g*)  C6H12(*g*) + H2(*g*) Endothermic!  C6H12(*g*)  C6H6(*g*) + 3H2(*g*) Endothermic!  toluene  benzene + methane**  **Catalyst: Pt/Re/Ge/Sn on Al2O3 support** |
| **#17** | **Ethyl Benzene**  **9 billion lbs** | **C6H6(*g*) + C2H4(*g*)  C6H5C2H5**  **1. Catalyst: Liquid phase system with AlCl3**  **2. Catalyst: Zelolite – Lewis Acid based gas phase process**  **Classic Friedel-Crafts rxn.** |
| **#19** | **Vinyl Chloride**  **8 billion lbs** | **ClCH2CH2Cl(*g*)  H2C=CHCl(*g*) + HCl(*g*)**  **This reaction is often coupled with the oxychlorination reaction to produce dichloroethane, this allows recycling of the HCl.** |
| **#20** | **Styrene**  **8 billion lbs** | **Dehydrogenation of ethyl benzene**  **Catalyst: Fe oxides on Al2O3 support**  **Conditions: 550-600°C** |
| **#21** | **Terephthalic Acid**  **8 billion lbs** | ***Amoco Process:* p-CH3-C6H4-CH3 + 3O2  p-HOOC-C6H4-COOH + H2O**  **Catalyst: Co/Mn salts (with some heavy metal bromides)**  **Conditions: liquid acetic acid solution, 200°C, 20 atm  Ti or Hastelloy C lined reactor (very corrosive)** |
| **#22** | **Methanol**  **7 billion lbs** | **CO + H2  CH3OH**  **Catalyst: ZnO/Cu salt**  **Conditions: > 100 atm, 200-300°C** |
| **#24** | **Ethylene Oxide**  **6 billion lbs** | **C2H4(*g*) + ½O2  ethylene oxide**  **Catalyst: Ag**  **Conditions: 300°C** |
| **#26** | **Toluene**  **6 billion lbs** | **Catalytic Reforming of methyl cyclohexane and derivatives**  **Catalyst: Pt/Re on Al2O3 support**  **Conditions: 500°C and 25 atm** |
| **#27** | **Xylenes**  **5.5 billion lbs** | **Catalytic Reforming of 1,4-dimethylcyclohexane**  **Catalyst: Pt/Re on Al2O3 support**  **Conditions: 500°C and 25 atm** |
| **#28** | **Ethylene Glycol**  **5 billion lbs** | **ethylene oxide + H2O  HOCH2CH2OH**  **Catalyst: H2SO4 (0.5 - 1%), 50°-70°C**  **Conditions: Thermal @ 195°C and 15 atm.** |
| **#29** | **Butylaldehyde**  **5 billion lbs** | ***Hydroformylation* -- Union Carbide/Celanese/BASF**  **propylene + H2 + CO  CH3CH2CH2CHO**  **Catalyst: *homogeneous* Rh/PPh3 catalyst**  **Conditions: 100-125°C, 8-25 atm** |
| **#31** | **Cummene**  **3.7 billion lbs** | **benzene + propene  C6H5CH(CH3)2**  **1. Liquid phase catalysts: H2SO4, AlCl3, HF**  **2. Gas phase catalyst: H3PO4 on SiO2**  **Friedel Crafts reaction**  **Conditions: 35-40ºC, 7 bar (liquid); 200-300ºC, 20-40 bar (gas)**  **Cumene is mainly used to produce phenol and acetone.** |
| **#32** | **Acetic Acid**  **3.5 billion lbs** | **CH3OH + CO  CH3COOH**  **Catalyst: *homogeneous* RhI2(CO)2   (*Monsanto Acetic Acid process*)**  **Conditions: 150°C, 35 atm** |

**Homogeneous Catalysis**

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[*catalyst*]

**A + B  C**

Remember that thermodynamics and equilibrium still rule!! A catalyst only speeds up the rate at which a chemical reaction reaches equilibrium. The actual equilibrium constant (thermodynamics) is NOT affected by the catalyst. Therefore, non-spontaneous reactions are usually NOT suitable for catalytic applications.

**Advantages/Disadvantages of Homogeneous Catalysts Relative to Heterogeneous Catalysts**

Good **homogeneous** catalysts are:

***good*** generally far more selective for a single product

far more active

far more easily studied from chemical & mechanistic aspects

far more easily modified for optimizing selectivity

***bad*** far more sensitive to permanent deactivation

far more difficult for acheiving product/catalyst separations

***Heterogeneous*** catalysts dominate chemical and petro­chemical industry: ~ 95% of all chemical processes use ***heterogenous*** catalysts.

**Homogenous catalysts** are used when ***selectivity*** is critical and product-catalyst ***separation problems*** can be solved.

**Homogeneous** or ***Heterogeneous***?

Because many **homogeneous** catalysts decompose to form ***heterogeneous*** catalysts, and some ***heterogeneous*** catalysts can dissolve to form **homogeneous** catalysts, one should always be careful about making assumptions on what type of catalyst one is using in any new catalytic experiment. There are several general ways to test whether a catalyst is **homogeneous** or ***heterogeneous***.

1. Exposure to elemental Hg will generally poison a ***heterogeneous*** catalyst
2. Exposure to polythiols will poison most **homogeneous** catalysts
3. Light scattering studies to identify the presence of colloids (***heterogeneous***)
4. Product selectivity studies

e.g., polymer bound alkenes:



|  |  |  |
| --- | --- | --- |
| **Catalyst** | ***Homo*/Hetero** | **% Yield** |
| RhCl(PPh3)3 | ***homo*** | 100 |
| Ni(OAc)2 + NaBH4 | **hetero** | -- |
| [Rh(nbd)(PR3)2]+ | ***homo*** | 90 |
| Pd/C | **hetero** | -- |
| [Ir(cod){P(i-pr)3}(py)]+ | ***homo*** | 100 |

Some Catalysis Terminology

***Turnover (TO)*** -- one loop through the catalyst cycle. Typically one equivalent of reactant is converted to one equivalent of product (per equivalent of catalyst).

***Turnover Frequency (TOF) or Turnover Rate*** -- the number of passes through the catalytic cycle per unit time (typically sec, min or hrs). This number is usually determined by taking the # of moles of product produced, dividing that by the # of moles of catalyst used in the reaction, then dividing that by the time to produce the given amount of product. The units, therefore, are usually just *time*1. Note that the rate of a batch catalytic reaction is fastest at the very beginning of when the reactant concentration is the highest and generally slows down as the reaction proceeds -- stopping when all the reactant is used up. Note the graph below for the production of aldehyde product from the homogeneously catalyzed reaction of vinyl acetate, H2, and CO.



The TOF, therefore, will generally vary throughout the course of a batch reaction. The ***Initial TOF*** is defined as the initial part of a catalytic reaction where the rate is the fastest and essentially linear. A far better measure of rate is the observed rate constant ***k***obs, which allows one to reproduce the entire product production curve given a set of reactant & catalyst concentrations. In the above graph, the reaction is pseudo-first order in excess reactant alkene (vinyl acetate concentration ~ 0.6 M, catalyst 0.3 mM) and ***k***obs is determined from a *ln* plot of the change in H2/CO pressure (reactant concentration) versus time for this rxn. When reporting ***k***obs chemists often normalize it to a certain catalyst concentration (1 mM, for example).

***Turnover Number (TON)*** -- the absolute number of passes through the catalytic cycle before the catalyst becomes deactivated. Academic chemists sometimes report only the turnover number when the catalyst is very slow (they don’t want to be embarassed by reporting a very low TOF), or decomposes quite rapidly. Industrial chemists are interested in both TON and TOF. A large TON (e.g., 106 - 1010) indicates a stable, very long-lived catalyst. TON is defined as the amount of reactant (moles) divided by the amount of catalyst (moles) times the % yield of product. Authors often report mole % of catalyst used. This refers to the amount of catalyst relative to the amount of reactant present. 10 mole % = 10 TO, 1 mole % = 100 TON, 0.01% = 10,000 TON.

***ee (enantioselectivity)*** – this defines the enantioselectivity of an asymmetric catalyst that produces more of one optically active enantiomer (*R* enantiomer, for example) than the other (*S* enantiomer). **ee** is defined as:



A catalyst that makes an equal amount of *R* and *S* enantiomers has 0% ee (a racemic mixture). 85% or higher is generally considered a good ee, although that depends on what the best known catalyst can do relative to that being reported.

Catalysis Data in Publications

There is a lot of mediocre/bad catalysis reported all the time in chemistry publications. One often has to dig into the data to figure this out. The things one wants to typically look for to tell whether there is “good” catalysis or not include:

1) # of turnovers performed – more is better

2) TOF (turnover frequency) – faster is better

3) Good selectivity for the product – this includes chemoselectivity, regioselectivity, and enantioselectivity (if applicable)

4) Reaction conditions – harsh? Mild? Unusual? Concentrations?

To figure out the number of turnovers you need to know the amount of substrate (reactant) and catalyst:



But authors often list these values in different ways and you may have to do some interpreting. The most common alternate way of representing the substrate:catalyst ratio is **mole %**. This is especially common for organic chemists doing Pd-catalyzed coupling reactions. 10 mole % catalyst means that there is 10% as much catalyst as substrate on a molar basis. This is equivalent to 10 turnovers.

10 mole % catalyst = 10 turnovers

*These represent the theoretical maximum # of turnovers. One also has to note the % yield or the % conversion of substrate into product to figure out the actual # of turnovers!!*

5 mole % catalyst = 20 turnovers

1 mole % catalyst = 100 turnovers

0.1 mole % catalyst = 1000 turnovers

0.01 mole % catalyst = 10,000 turnovers

**Example:** Consider the following catalytic data reported in a *J. Am. Chem. Soc.* communication (very prestigious) *J. Am. Chem. Soc.* **1990**, *112*, 2803.:



Insert Table 1 from the paper here.

Let’s look at the last line of data from the table since that had the highest ee. The third column contains the important information about the ratio of reactant (often referred to as substrate), chiral chelating ligand L\*, and PdCl2.

The authors had 7.7 equivalents of reactant, 0.38 equivalents of chiral ligand, and 1 equivalent of Pd. This means that the maximum number of turnovers they could do is defined by the amount of reactant (moles or equivalents) divided by the amount of catalyst (moles or equivalents).



7.7 turnovers is small and not at all impressive. Hydrocarboxylation, however, is a very difficult catalytic reaction and doing it asymmetrically is even more impressive.

Of course, 7.7 turnovers assumes 100% yield, which they did not get. The actual number of turnovers needs to be reduced by the % yield, which they report as 64%, so the actual number of turnovers is:



4.9 turnovers is barely catalytic. What about the TOF? Well you have to read a little footnote to find how long they ran the reaction to get their 64% yield: 18 hours at 1 atm of CO. The TOF is the number of turnovers divided by the time:



Well, 0.27 turnovers/hr is also barely catalytic. But that 91% ee is quite impressive isn’t it. Or is it?

The authors only added 0.38 equivalents of chiral ligand to 1 eq of PdCl2 to generate, at most, 0.38 equivalents of chiral catalyst (assuming one ligand per Pd). This is rather unusual, since one usually adds a little excess of chiral ligand to generate a chiral catalyst, even when dealing with a chelating ligand. There are examples where one can add less ligand than metal complex due to the fact that the metal-ligand catalyst generated is much more active than the starting metal complex itself. But one almost always adds enough ligand (or extra since the ligand can dissociate) to generate as much of the presumed catalytically active species as possible.

The ligand that the author is using is:



This is being used under rather acidic conditions (typically needed for Pd-catalyzed hydrocarboxylation) and under these conditions it is highly unlikely that it would be able to function as a ligand. Remember that the late transition metals don’t particularly like oxygen donor ligands (weaker bonding).

This fact makes the high ee’s rather suspect. And a number of industrial research groups (Hoechst Celanese, Union Carbide, Albemarle) have found (although not published) that the actual ee for this “catalyst” is close to 0.

So it is often important to read the experimental conditions very carefully and with a critical eye.

Problem: Consider the following catalytic data reported in a recent publication (*Chem. Commun.* **1999**, 25). What information is missing?

Insert Table 1 from the paper here.

Insert the Notes and references from the paper here.

Problem: Beller and coworkers have reported (*Angew. Chem.*, **2001**, *40*, 3408.) on hydroformylation catalysis using HRh(CO)(Naphos). The table of catalytic data from their paper is shown below. For experiment # 1, how many turnovers did the authors do? Clearly show how you calculate your number. Is there any important data missing from this table?

Insert Table 1 from the paper here.

**Problem:** What information is missing from the following Table of catalytic results (they defined the ligands used elsewhere in the paper). How many turnovers are they doing (*Tetrahedron Lett.* **2002**, *43*, 4977)?

Insert Table 1 from the paper here.