UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

GREEN CHEMISTRY

CATALYSIS

Image: Flickr, Catalysts, Author: BASF Catalysts

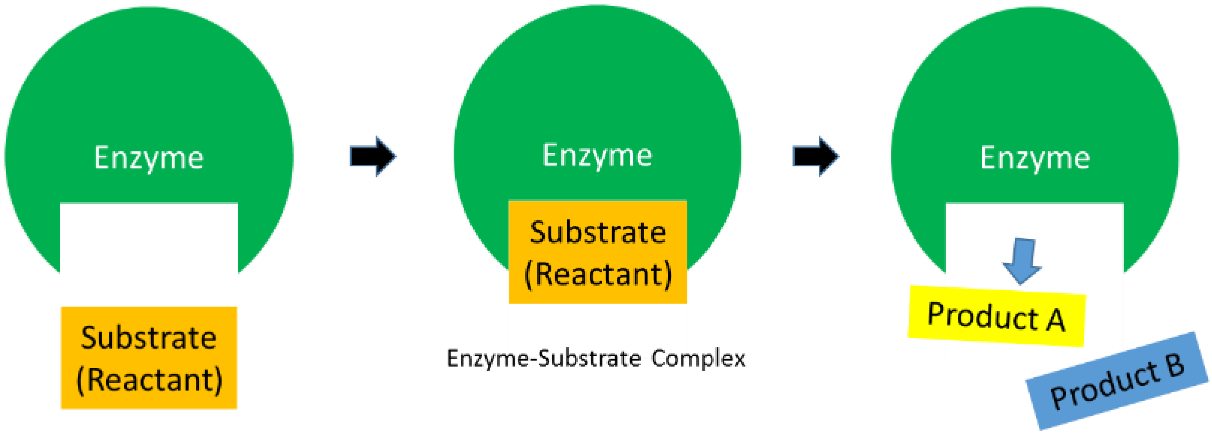
DAY 3 SESSION I
4-DAY PRESENTATION

www.greenchemistry-toolkit.org

Topics To Be Covered

1. Activation Energy for Reaction
2. What is a Catalyst?
3. Types of Catalysts
4. Catalysts and Sustainability
5. Important Improvements Using Catalysts
6. Enzymatic Reactions
7. Examples and Considerations

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.



ACTIVATION ENERGY FOR REACTION

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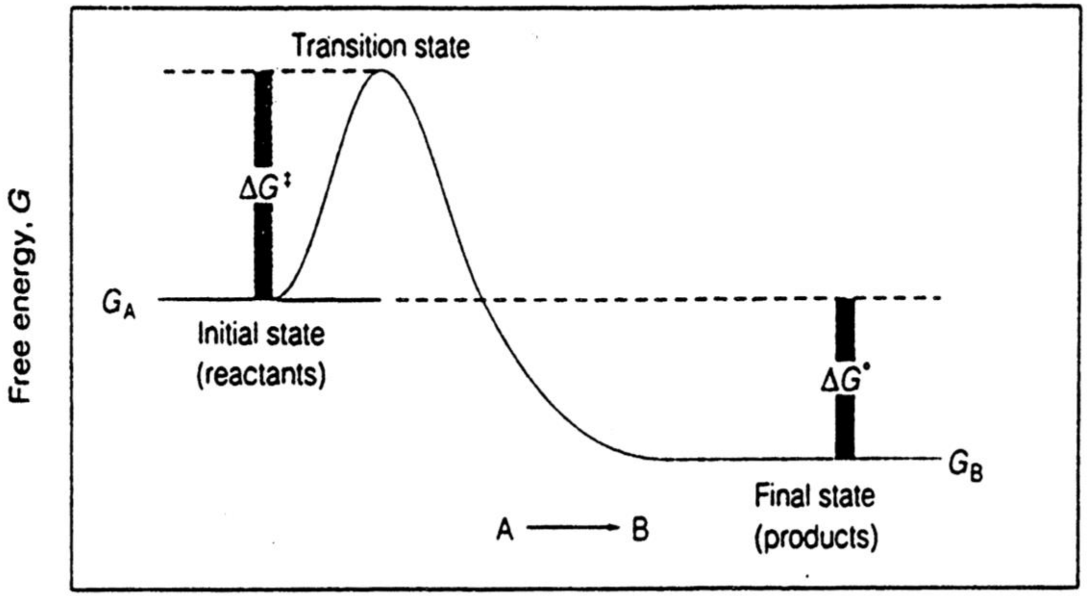
- Molecules must be activated before they can undergo a reaction.
  - Reactants must absorb enough energy from their surroundings to destabilize chemical bonds (the energy of activation).
- Transition state
  - The intermediate stage in a reaction where the reactant molecule is strained or distorted but the reaction has not yet occurred.

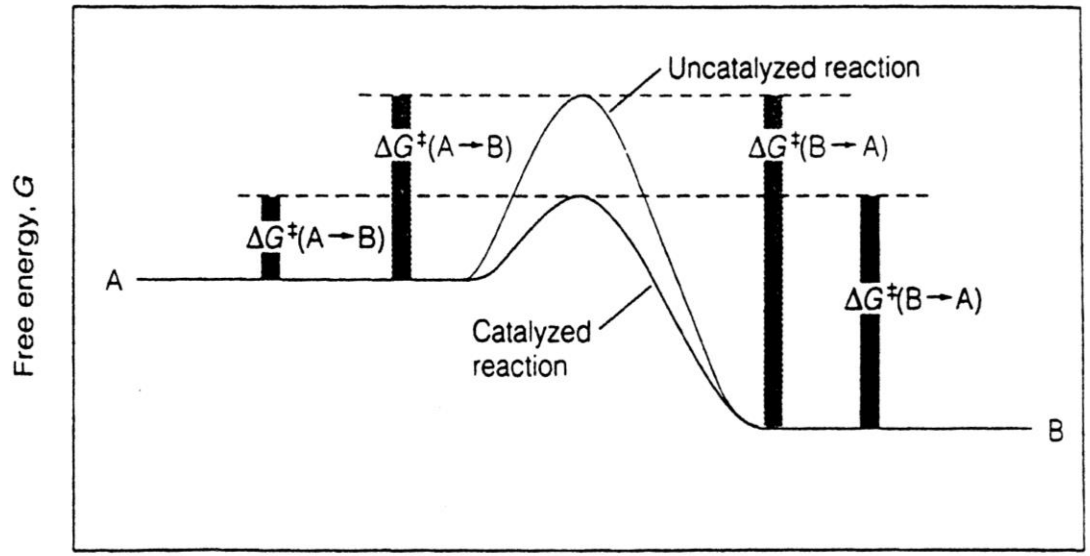


ACTIVATION ENERGY FOR REACTION

- A catalyst lowers the energy of activation by:
  - Forcing molecules into conformations that favor the reaction.

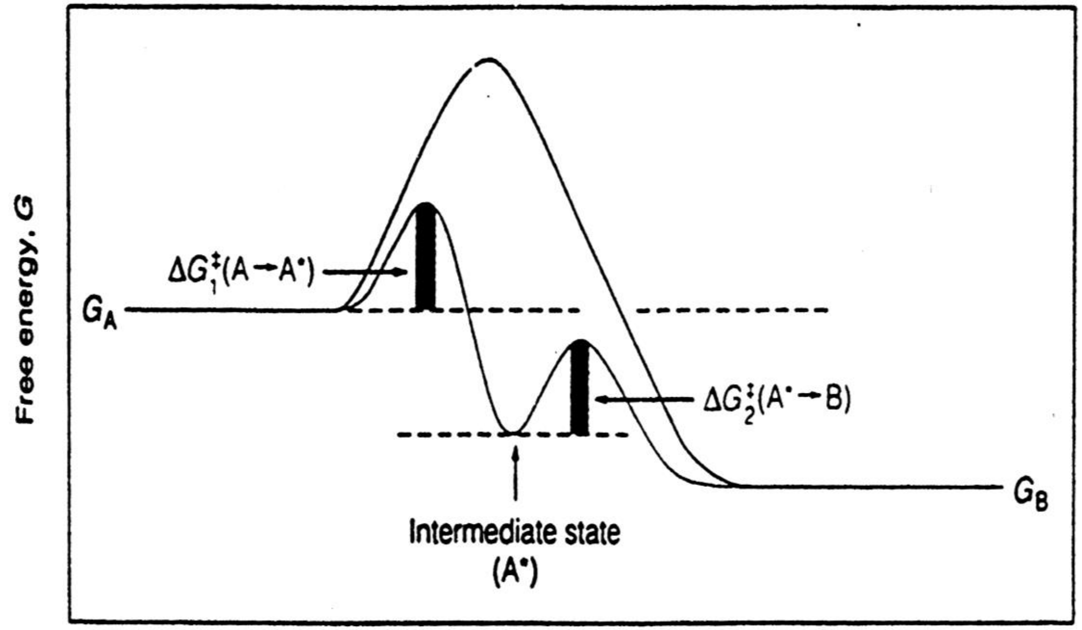
    I.e. the catalyst may re-orientate molecules.
- The change in free energy is identical to the uncatalyzed reaction:

  The catalyst does not change the thermodynamic equilibrium.



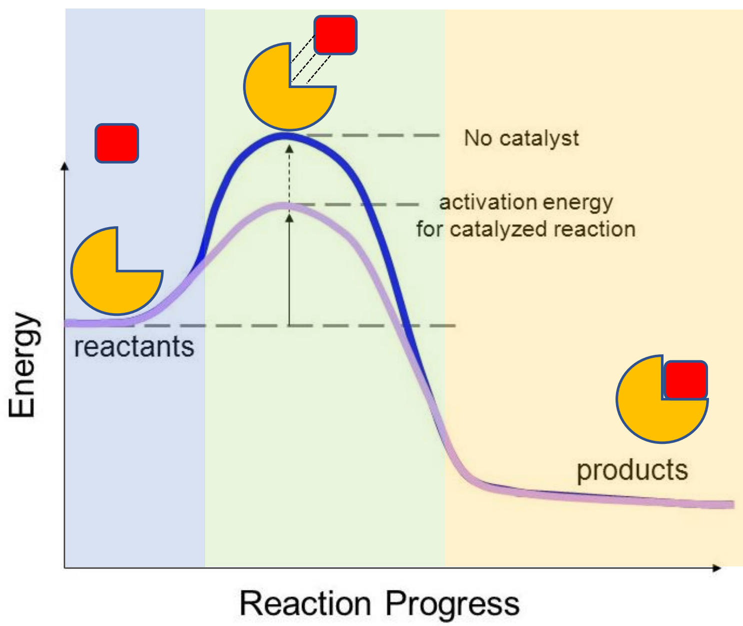
ACTIVATION ENERGY FOR REACTION

- Sometimes catalysts cause one large energy barrier to be replaced by two smaller ones.
  - The reaction passes through an intermediate stage.



WHAT IS A CATALYST?

A catalyst is a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.



Source: Wikipedia

Some Advantages of using Catalysts:

- They lower the activation energy of the reaction.
- They can be recycled and reused.
- They are used in minuscule amounts.
- Using them shortens the reaction time.

TERMINOLOGY: HETEROGENEOUS AND HOMOGENEOUS CATALYSTS

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An ideal green catalyst would have a preferred parameters from each type.

		Homogeneous	Heterogeneous
Form	Form	Soluble metal complexes, usually mononuclear	Metals, usually supported, or metal oxides
Active site	Active site	Well-defined, discrete molecules	Poorly defined
Temperature	Temperature	Low (<250^{o}C)	High (250 – 500°C)
Selectivity	Selectivity	High	Low
Product separation	Product separation	Generally problematic on large scale	Facile
Green?	Green?	Less Green	More Green Separation, Recycle/Regeneration

TERMINOLOGY: CRYSTALLINE MICROPOROUS CATALYSTS

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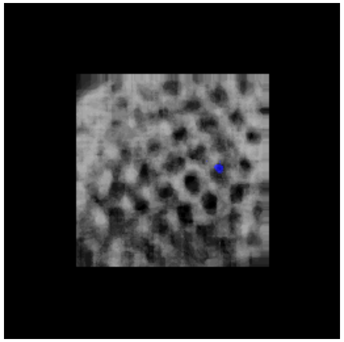
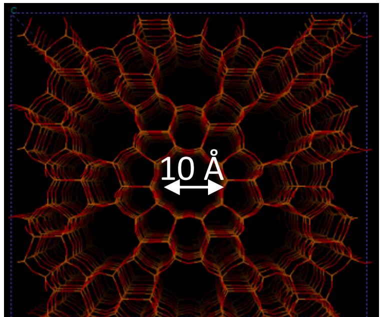
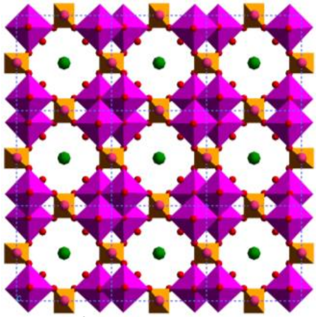
- ❑ Regular crystalline structure.
- ❑ Porous on the scale of molecular dimensions.
  - 10 – 100 Å
  - Up to 1000's m^2/g surface area
- ❑ Catalysis through:
  - Shape selection.
  - Acidity/Basicity.
  - Incorporation of metal particles.

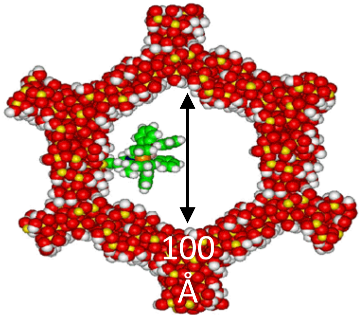




Zeolite (silica-aluminate)



Silico-titanate



MCM-41 (mesoporous silica)

TERMINOLOGY: AMORPHOUS HETEROGENEOUS CATALYSTS

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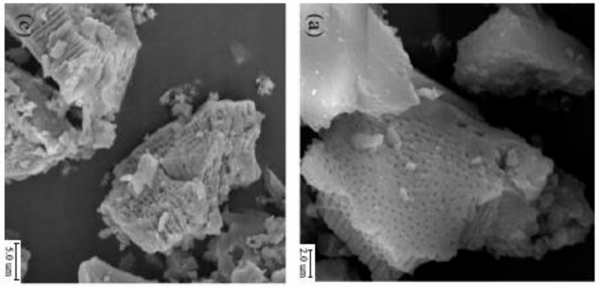
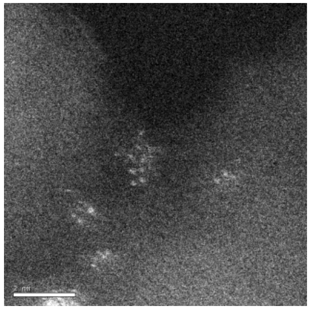
- Amorphous, high surface area supports:
  - Alumina, silica, activated carbon, and many more.
  - Up to 100’s of m^2/g of surface area.
- Impregnated with catalytic transition metals:
  - Such as Pt, Pd, Ni, Fe, Ru, Cu, and Ru.
- Typically pelletized or on monoliths.
- <u>Cheap</u>, high stability, and can catalyze many types of reactions.
- Most used, but the least well understood of all classes of catalysts.



SEM micrographs of alumina and Pt/alumina



TERMINOLOGY: TURNOVER FREQUENCY AND SELECTIVITY

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Turnover Frequency, TOF (s^{-1})

The amount of molecules transformed form per given time = the rate of reaction.

Inorganic Catalyzed Reaction	Enzymatic Reactions
0.01 – 10000 s^{-1} (Very slow)	100 up to 40 million s^{-1} (Extremely fast)

Selectivity (%)

To form one product exclusively despite the presence of other possibilities.

A + B --------------> C + D + E

C	D	E	
100 mole	0 mole	0 mole	Selectivity for C = 100%

C	D	E	
33 mole	50 mole	17 mole	Selectivity for C = 33% Selectivity for D = 50% Selectivity for E = 17%

CATALYSTS ARE WIDELY USED BY INDUSTRY AND BY NATURE

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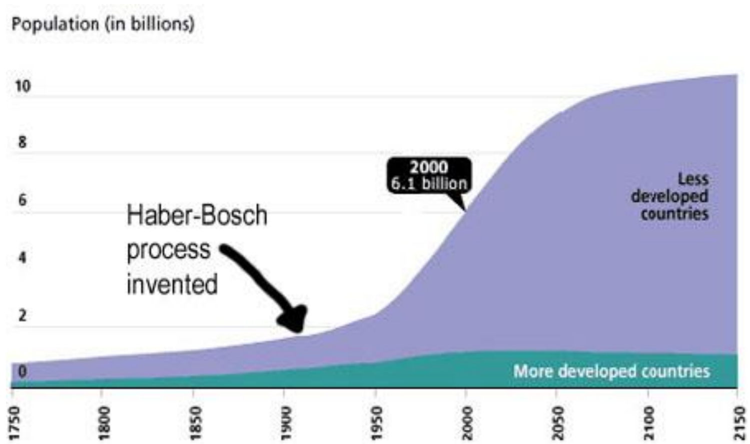
Catalyst	Reactions catalyzed
Iron oxide	Ammonia from nitrogen and hydrogen
Chromium-Molybdenum Alloy Nickel-Molybdenum Alloy Zeolite (Porous Aluminum and Silica Oxide)	Petroleum Industry
Acid (HCl, H_2SO_4, HNO_3)	Many organic reactions
Enzymes	Starch into sugars and sugars to ethanol



Source: Wikipedia

The Haber-Bosch process, which allows fertilizer production, is facilitated by a catalyst.

The invention of the process led to a global increase in human population.

CATALYSIS DRIVES THE CHEMICAL INDUSTRY

GREEN CHEMISTRY

Petroleum

Fine chemicals

Consumer Products

Pharmaceuticals

Catalytic processes contribute to more than 35% of global GDP.

Source: Wikipedia

IMPORTANT HETEROGENEOUS CATALYTIC PROCESSES

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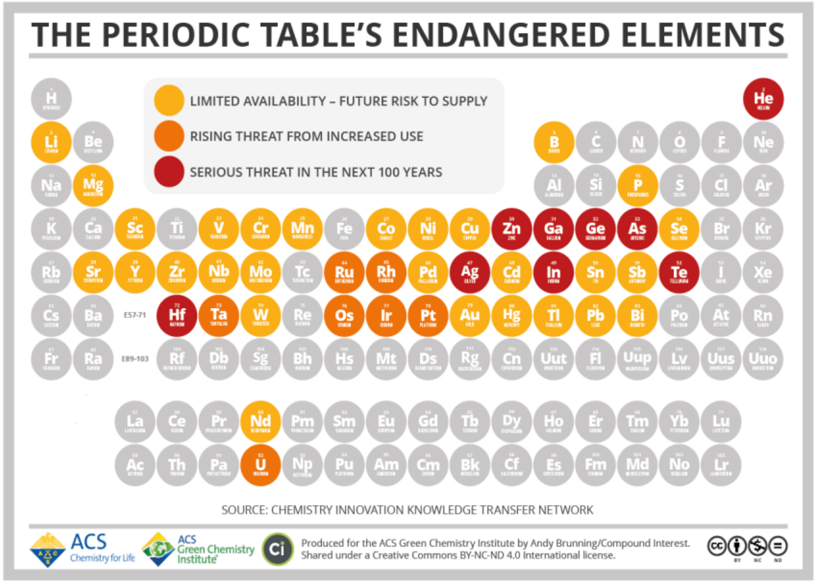
- **Haber-Bosch process:**
  - $N_2 + 3\ H_2 \rightarrow 2\ NH_3$
  - Fe/Ru catalysts, high pressure and temperature.
  - Critical for fertilizer and nitric acid production.
- **Fischer-Tropsch chemistry:**
  - $n\ CO + 2n\ H_2 \rightarrow (CH_2)_n + n\ H_2O$, *syn* gas to liquid fuels.
  - Fe/Co catalysts.
  - Source of fuel for Axis in WWII.
- **Fluidized catalytic cracking:**
  - High MW petroleum → low MW fuels, like gasoline.
  - Zeolite catalysts, high temperature combustor.
  - Likely in your fuel tank.
- **Automotive three-way catalysis:**
  - $NO_x/CO/HC \rightarrow H_2O/CO_2/H_2O$
  - Pt/Rh/Pd supported on ceria/alumina.
  - Makes exhaust 99% cleaner.

DESIGNING A GREEN CATALYST

GREEN CHEMISTRY

Not all catalysts are created equal. Chemists need to consider various factors when deciding on a catalyst.

- Is the catalyst non-toxic?
- Is it actually used in sub-stoichiometric amounts?
- Does it require special conditions (sensitivity to solvent, moisture, oxygen)?
- Is it derived from abundant/renewable resources?
- Can it be reused?
- Can it be separated from the products?
- Might it lead to dangerous conditions (Runaway/chain reactions)?

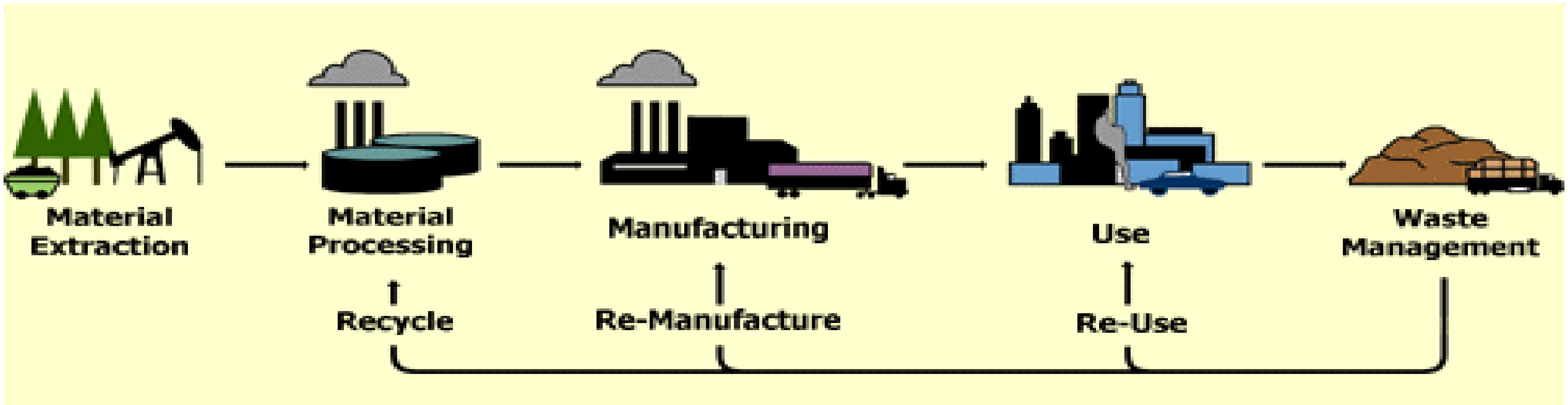


Many metals which are used as catalysts are quickly depleting.

http://www.rsc.org/chemistryworld/Issues/2011/January/CriticalThinking.asp

USE A LIFECYCLE AS A GUIDE

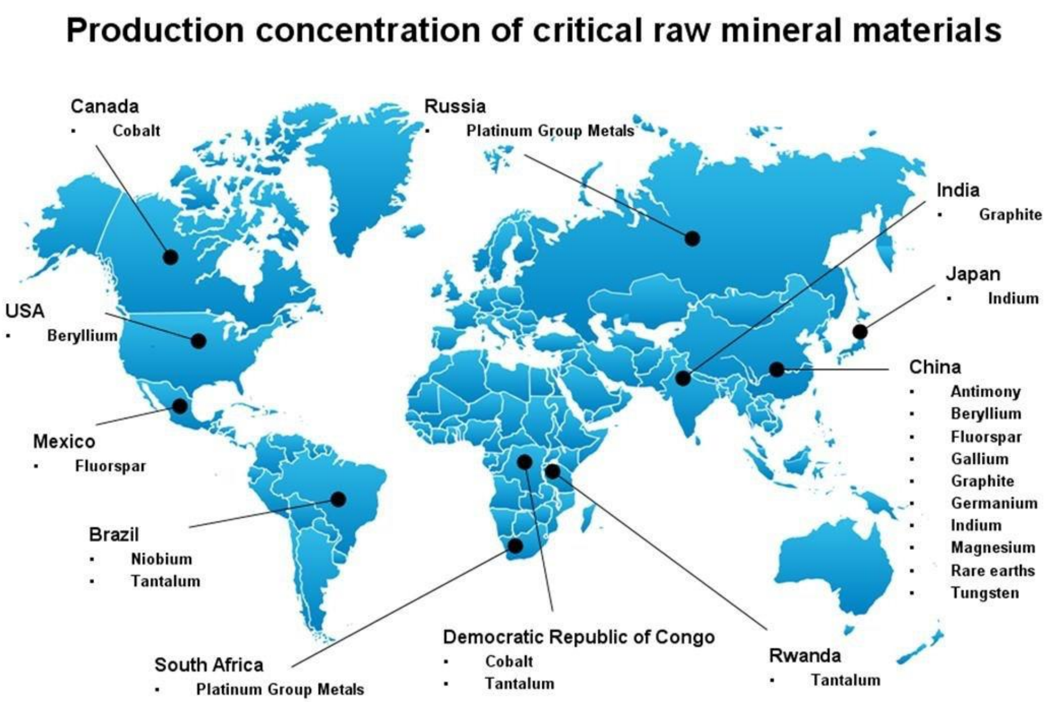
GREEN CHEMISTRY



- **Material Extraction**
  - Abundance?
- **Processing/Manufacturing**
  - Energy?
  - Waste?
  - Toxicity of materials?
- **Use**
  - Selectivity?
  - Turnover number?
  - Safety?
- **End-of-life**
  - Reusability?
  - Ease of separation?

THE NEED TO DEVELOP MORE SUSTAINABLE CATALYSTS

GREEN CHEMISTRY



European Commission Press Release, June 2010

Raw materials (e.g. rare precious metals) are dispersed around the world and access to them is frequently political.

To gain economic and environmental independence, we must design catalysts which are locally sourced and abundant.

CURRENT TRENDS IN CATALYST DESIGN

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Reduce Loading

- High Surface Area Support
- Atomic Layer deposition

Earth Abundant Alternatives

- Abundant metal
- Alloy - Synergistic Effect
- Adjust other parameters
  - Solvents
  - Surfactants

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EXAMPLE: THE HABER-BOSCH PROCESS

Improving the Haber-Bosch process by using an iron catalyst:

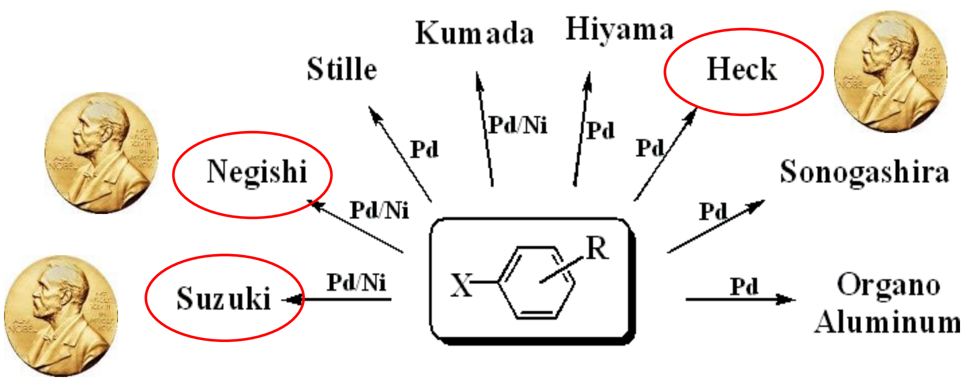
$$N_2 + 3H_2 \rightarrow 2NH_3$$

Group→ ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			** 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

- Traditionally the H-B reaction was made using Osmium metal as catalyst.
  - Osmium metal is rare and toxic, which made the reaction unsustainable.
- Because Iron is in the same column as Osmium, its properties are similar.
- (Fe_3O_4) is an alternative catalyst that will provide a comparable yield.

Cross Coupling Reactions:

→ Connecting two separate organic molecules together with high selectivity and high yield.



	USD mol^{-1}
Ni	\$1.20
Pd	\$1,500

New chemistry innovations allowed the replacement of expensive palladium catalysts with nickel.

These reactions were awarded Nobel Prizes.

OTHER CATALYST IMPROVEMENTS: ALLOYS

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In addition to moving away from precious metals, scientists can use metal alloys for synergistic effect:

- Alloying of multiple metals:
  - Bronze – Copper + Tin (or Zinc)
  - Monel – Copper + Nickel
  - Stainless Steel – Steel (Iron + C) + Chromium

    (with many other possibilities)
- The surface area:
  - Thin layer deposition
  - Ultra high area support

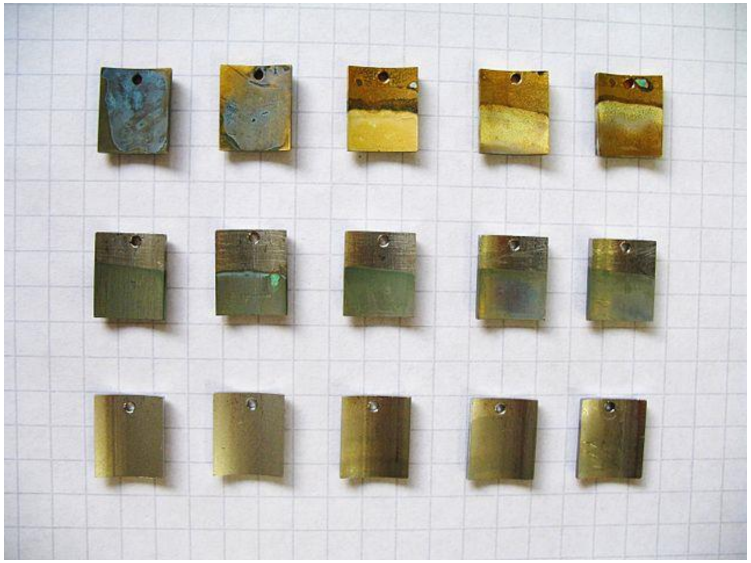


Image: Wikimedia Commons, Corrosion of alloys in NaCl, Author: Vvjbp

INCREASED SURFACE AREA

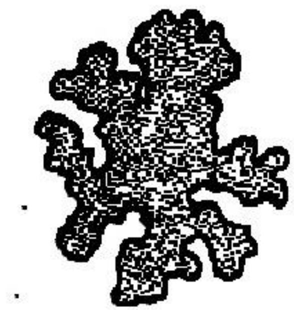
High surface area porous support:

$<50\ cm^2\ g^{-1}$

Non-porous solid

- Low specific surface area
- Low specific pore volume

$50 – 4000\ cm^2\ g^{-1}$

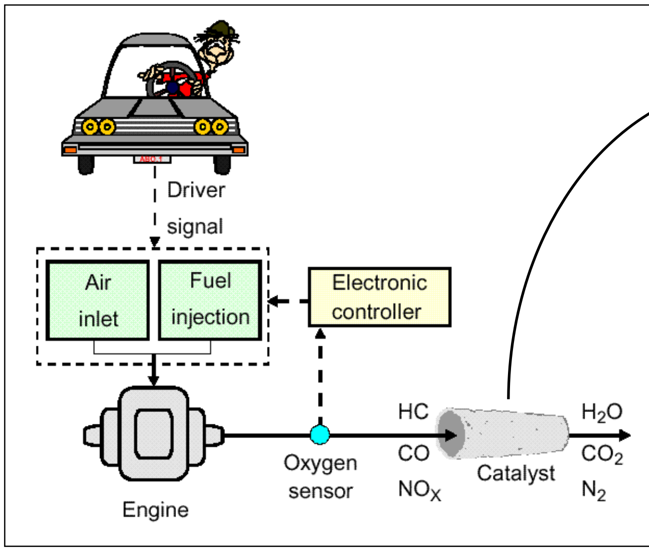


Porous solid

- High specific surface area
- High specific pore volume

Porous materials have highly developed internal surface area that can be used to perform a specific function. Almost all solids have some amount of porosity.

AUTOMOTIVE EMISSIONS CONTROL SYSTEM

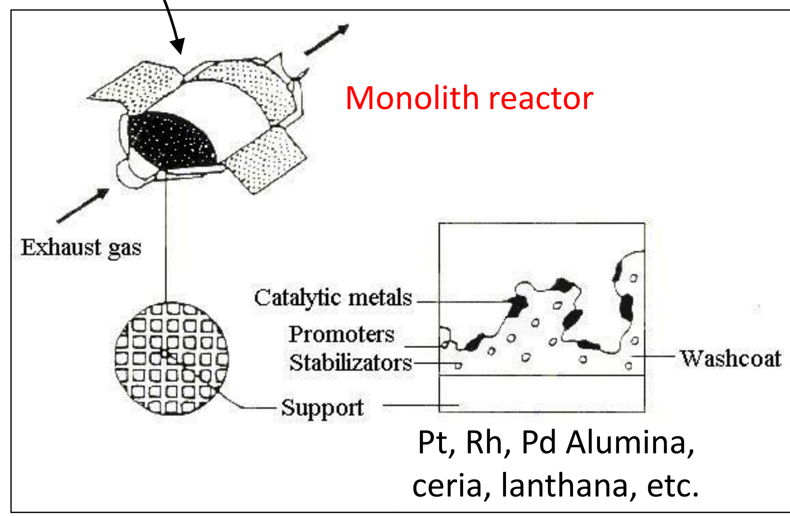


<u>"Three-way" Catalyst</u>

$CO \rightarrow CO_2$

$HC \rightarrow CO_2 + H_2O$

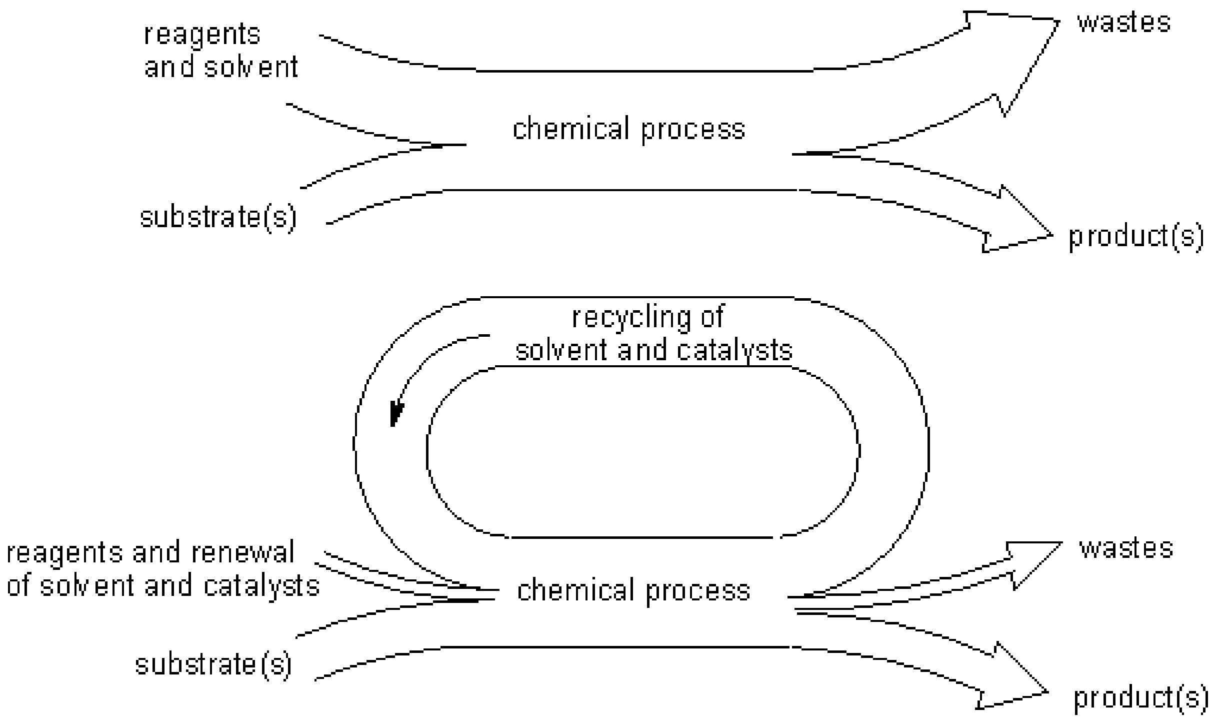
$NO_x \rightarrow N_2$



Most widely deployed heterogeneous catalyst in the world.
You probably own one!

TOWARDS GREENER CATALYSIS – FLOW CHEMISTRY

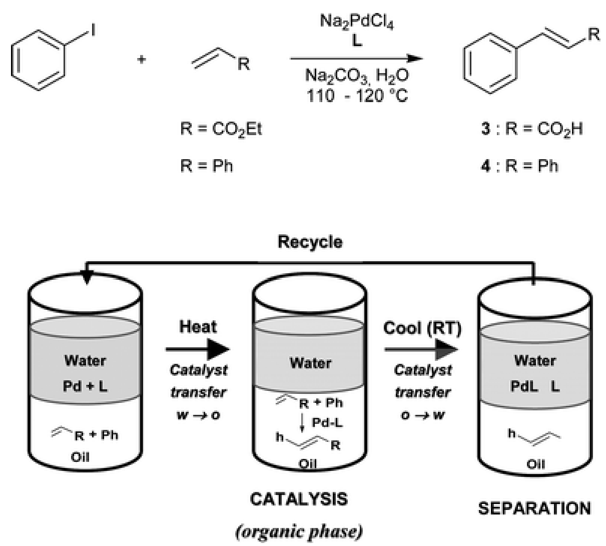
GREEN CHEMISTRY



http://www.organic-chemistry.org/topics/green-chemistry.shtm (Accessed on 4/1/2016)

Separation of the catalyst becomes a key drawback

Phase separation – takes advantage of the difference in Log P



Azoui H., Baczko K., Cassel S., Larpent C. *Green Chem*. **2008**, 10, *1197-1203*.

ENZYMATIC REACTIONS

GREEN CHEMISTRY

Enzymatically driven reactions that occur in nature are often highly specific and compartmentalized.

Many of these reactions occur in ambient temperature and pressure with a water solvent.

Today, over 5000 of enzymatic reactions types have been identified, and that number continues to grow.

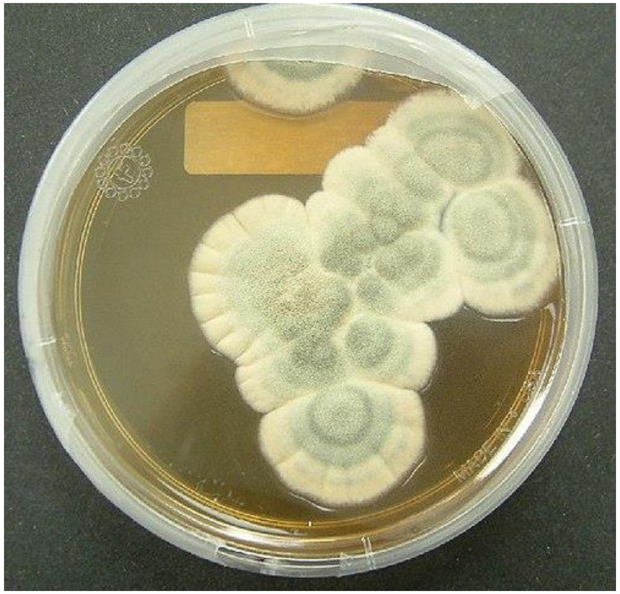
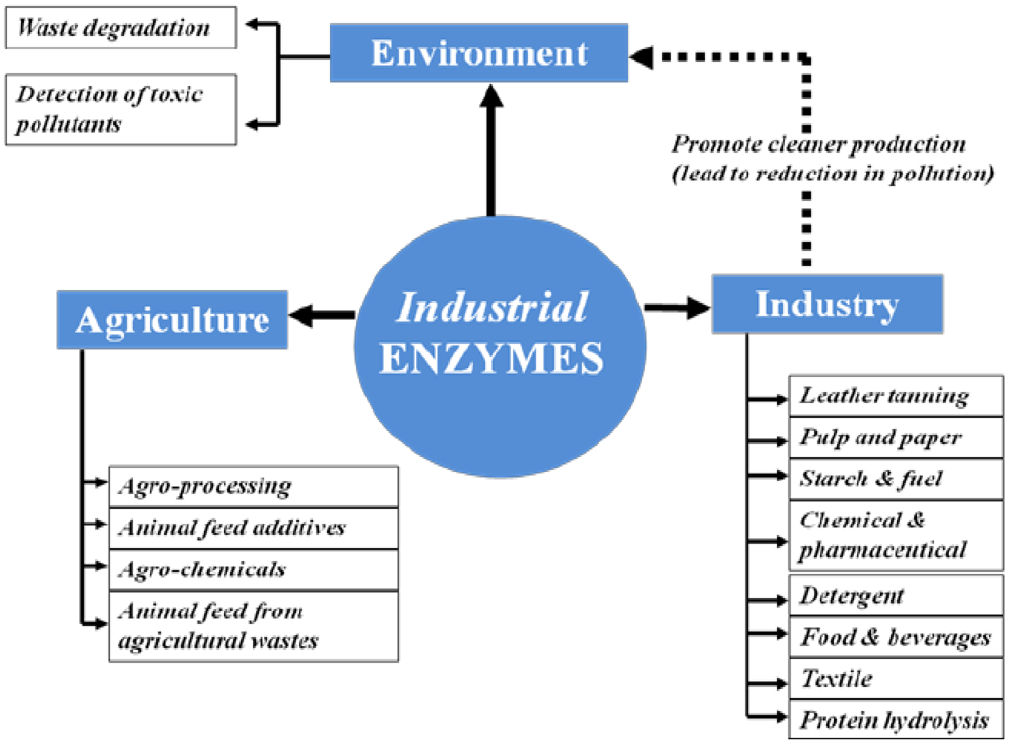


Image: Wikimedia Commons, Penicillium notatum,
Author: Crulina 98

ENZYMATIC REACTIONS

GREEN CHEMISTRY

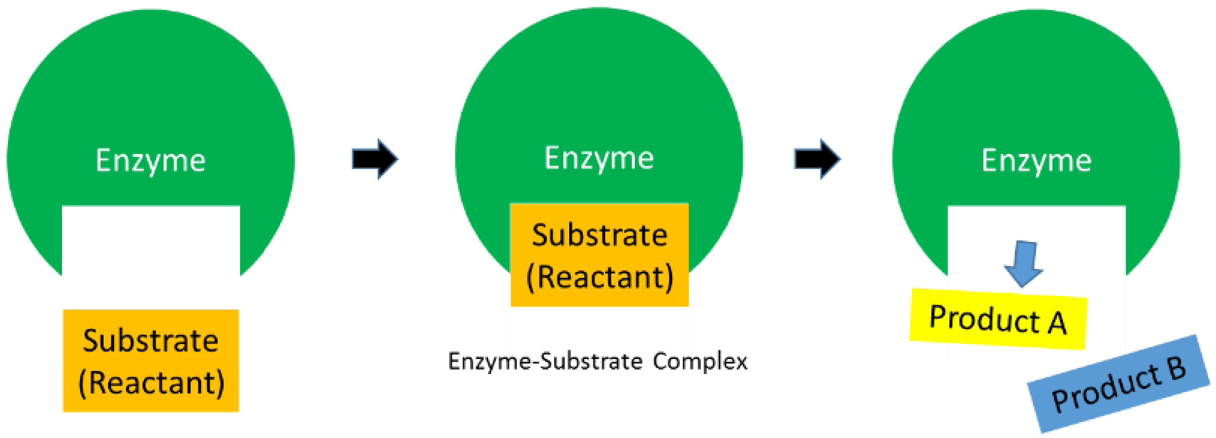
Enzymes are biological catalysts and are used in industry, agriculture, and by nature.



ENZYMATIC REACTIONS

GREEN CHEMISTRY

This is a general representation of enzymatic reactions – the lock and key mechanism.



The substrate (reactant) binds with the enzyme and forms the Enzyme-substrate complex and is transformed into products A and B, which are released from the active site upon reaction completion.

EXAMPLES ON ENZYMATIC CATALYSIS

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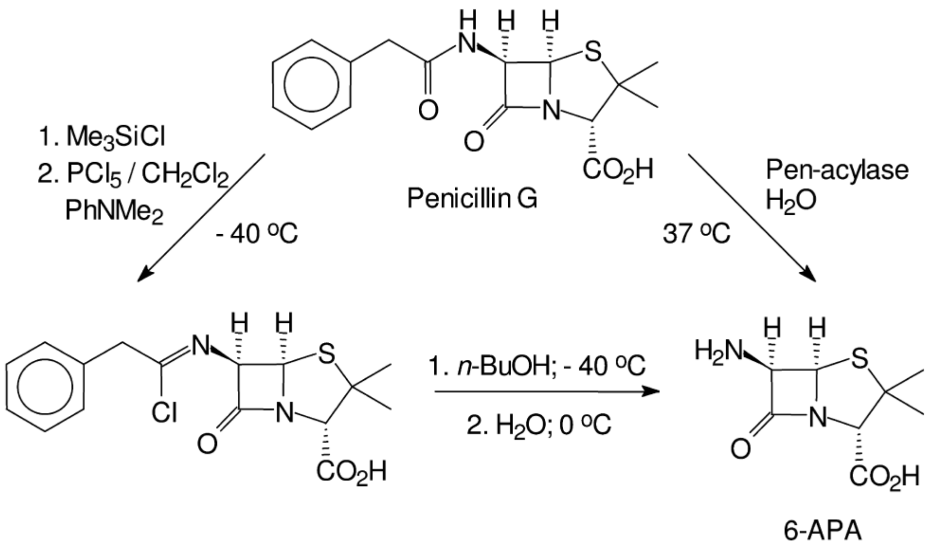

Conventional manufacturing of 6-aminopenicillanic acid (6-APA) - a key raw material for semi-synthetic penicillin and cephalosporin involved the use of environmentally unattractive reagents – requires a chlorinated hydrocarbon solvent and a reaction temperature of –40C.

In contrast, enzymatic cleavage of penicillin G is performed in water at 37C and the only reagent used is to adjust the pH.

The enzymatic process currently accounts for the majority of the several thousand tons of 6-APA produced annually on a world-wide basis.

CASE STUDY

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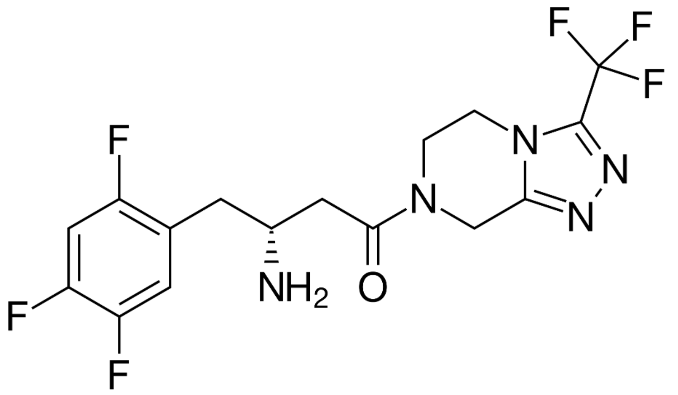
Sitagliptin – Rhodium to Enzyme

Sitagliptin is Merck's top-selling diabetes drug.

It brought $1.9 million in sales in 2009.

Traditional synthesis used high pressure and a heavy metal – rhodium.

The new improved synthesis with enzymes allows for 99.95% selectivity to the desired product and eliminates all heavy metal wastes.



Sitagliptin, the active ingredient in Merck's Januvia.

http://www.rsc.org/chemistryworld/News/2010/June/17061002.asp (Accessed on 4/1/2016)
Savile, C. K.; Janey, J. M.; Mundorff, E. C.; Moore, J. C.; Tam, S.; Jarvis, W. R.; Colbeck, J. C.; Krebber, A.; Fleitz, F. J.; Brands, J.; Devine, P. N.; Huisman, G. W.; Hughes, G. J., Biocatalytic Asymmetric Synthesis of Chiral Amines from Ketones Applied to Sitagliptin Manufacture. *Science* **2010,** *329* (5989), 305-309.

THE PROS AND CONS OF ENZYMATIC REACTIONS

GREEN CHEMISTRY

Pros:

- Mild conditions.
- Aqueous environment.
- Atmospheric conditions.
- A very specific and high reaction rate.

Cons:

- Separations are often complicated.
- They can be expensive to produce.
- Some people might experience allergic reactions to some enzymes.

TOPICS COVERED

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UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

GREEN CHEMISTRY

THANK YOU!

QUESTIONS?

This training material was developed in close collaboration with the Center for Green Chemistry and Green Engineering at Yale University.

www.greenchemistry-toolkit.org