Heterogeneous Catalysis and Green Chemistry

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Why Green Chemistry?

What is Green Chemistry?

How catalysts can make a process green?

Emergence of chemistry in the modern era

Chemistry has changed our lives ?

- An understatement – Chemistry has become part of our lives.
- There is practically no human activity that does not involve chemistry at some stage or the other.
- Food, transport, medicine, lifestyle- you name it-

Chemistry has become an all-pervading science.

The other side of the coin

- Even Chemistry could not defy the laws of physics and philosophy.
- Anything that grows out of proportion can also become out of control.
- Many unpleasant side effects and events.

Today this may appear as a funny picture
Tomorrow this may be a real scene

Result

- A negative perception of the public and opposition to new chemical plants.
- A steep decline in the number of people interested in higher education.
- Decline in R &D in chemistry, all over the world

- This warranted a strong legislation, public awareness and support, and above all, a different way of doing chemistry.
- And the Green Chemistry Movement was initiated

Action plan

- Accountability- Not gross, at the atomic level

Waste Management? minimization? –

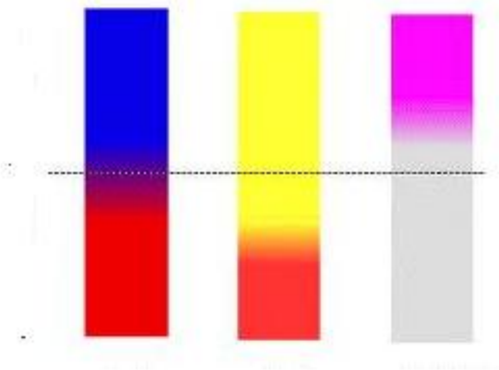
Not enough- Zero waste

- Optimized use of resources
- Mild conditions

Use of safer reagents and solvents

- Less number of process steps

Need for indicators



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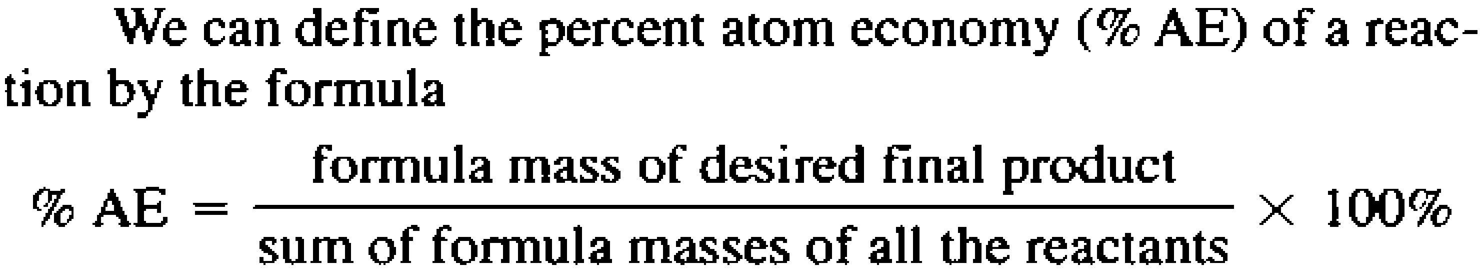
An indicator is a numerical measure used to show the progress toward achieving a specified outcome.

According to Lapkin (2002), a group of indicators selected in order to characterise a complex phenomenon constitute a METRIC

Atom Economy

The **Atom Economy** concept (Trost 1991) calculates how much of the reactants remain in the end of a chemical transformation.

The method ignores reaction yield and molar excess of reactants, neither accounts for solvents and reagents (Constable et al. 2002).



We can define the percent atom economy (% AE) of a reaction by the formula

$$\% \text{ AE} = \frac{\text{formula mass of desired final product}}{\text{sum of formula masses of all the reactants}} \times 100\%$$

It is TH “E” factor that counts

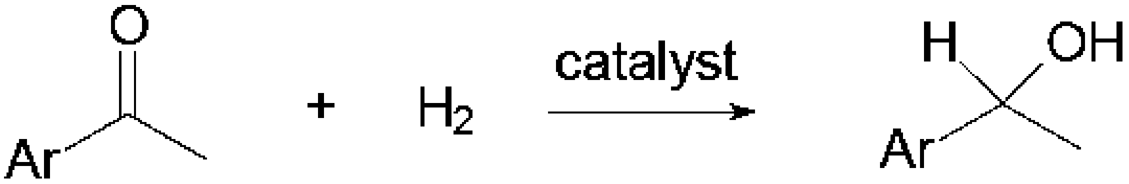
The Environmental (E) factor quantifies the mass of waste generated per mass of product (Sheldon 1994, 1997).

The specific hazard posed by different waste types is not taken into account.

Name	Definition	Units
Atom economy	$= \dfrac{\text{MW product x 100}}{\text{MW all reagents}}$	%
Effective Mass Yield (EMY)	$= \dfrac{\text{Mass product x 100}}{\text{Mass non-benign reagents}}$	%
E factor	$= \dfrac{\text{Mass waste}}{\text{Mass product}}$	kg/kg
Mass intensity (MI)	$= \dfrac{\text{Total mass}}{\text{Mass product}}$	kg/kg
Mass productivity	$= \dfrac{\text{Mass product x 100}}{\text{Total mass reagents}}$	%
Reaction Mass Efficiency (RME)	$= \dfrac{\text{Mass isolated product x 100}}{\text{Total mass reagents}}$	%
Carbon efficiency	$= \dfrac{\text{Mass carbon in product x 100}}{\text{Total mass carbon in reagents}}$	%

Atom Efficient Processes

Hydrogenation:



100% atom efficient

Carbonylation:

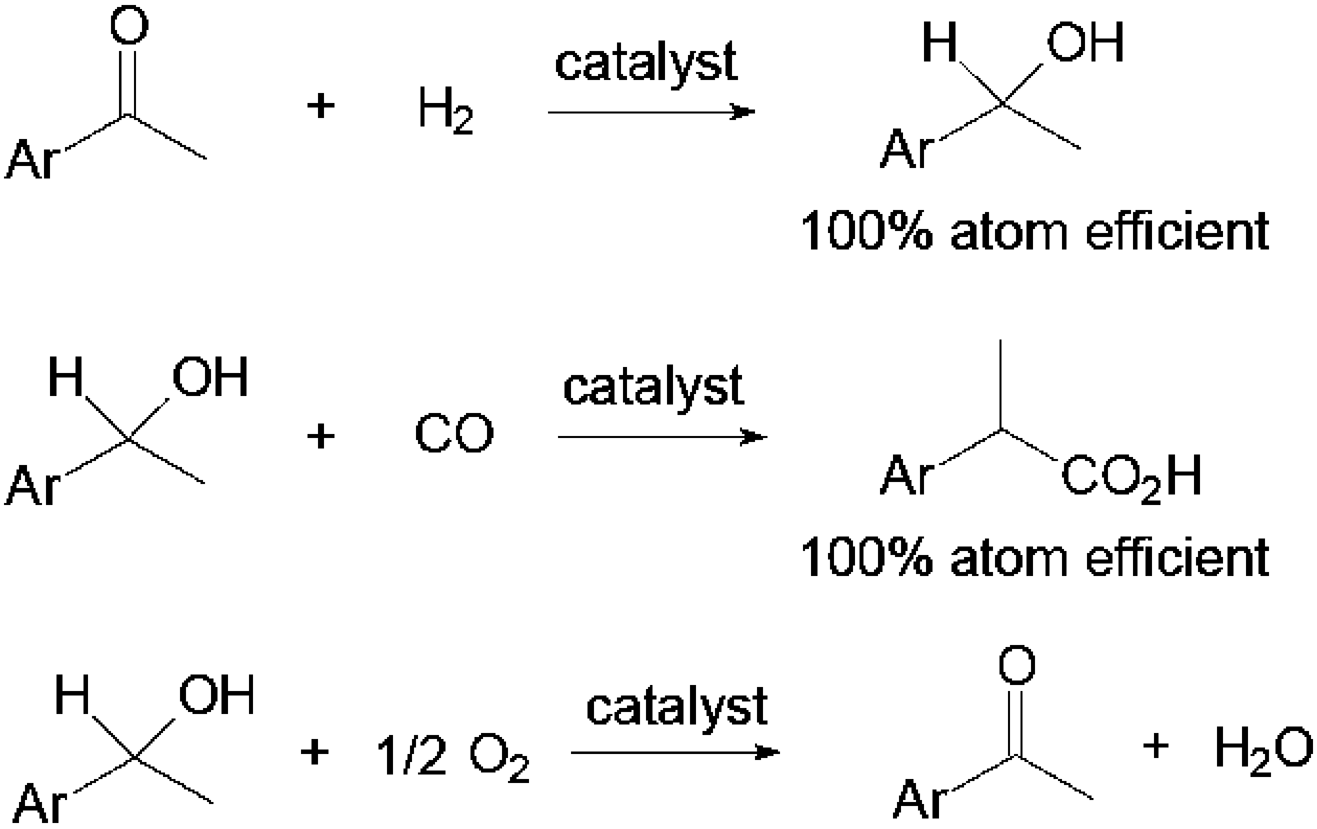
100% atom efficient

Oxidation:

87% atom efficient

(Ar = C_6H_5)

Atom efficient process



Hydrogenation:

100% atom efficient

Carbonylation:

100% atom efficient

Oxidation:

87% atom efficient

(Ar = C_6H_5)

Catalysis- to open the gates to Green World

Catalysis is a science at the interface between chemistry, physics, biology and materials science.

It enables chemical processes to be realized in a cost, energy and eco-efficient manner.

More than 80% of the processes in the chemical Industry worth approximately €1500 billion, depend on catalytic technologies.

- Catalysis is a science at the interface between chemistry, physics, biology and materials science.

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- More than 80% of the processes in the chemical Industry worth approximately €1500 billion, depend on catalytic technologies.

- The term **'catalysis**' was coined by Berzelius in 1836.

- He concluded that besides' Affinity' a new force is operative, the' Catalytic Force'.Reaction occurred by catalytic contact.

- The word 'catalysis' stems from the Greek – to 'loosen'.

- According to the **IUPAC (1976) –**
A catalyst is a substance that, being present in small proportions, increases the rate of attainment of chemical equilibrium, without itself undergoing a chemical change.

The reach of Catalysis

Household commodities

Gadgets

Energy Demand

Luxury

Health

Industrial Chemicals

All other Engg

Environment

Population

Alternative Fuels

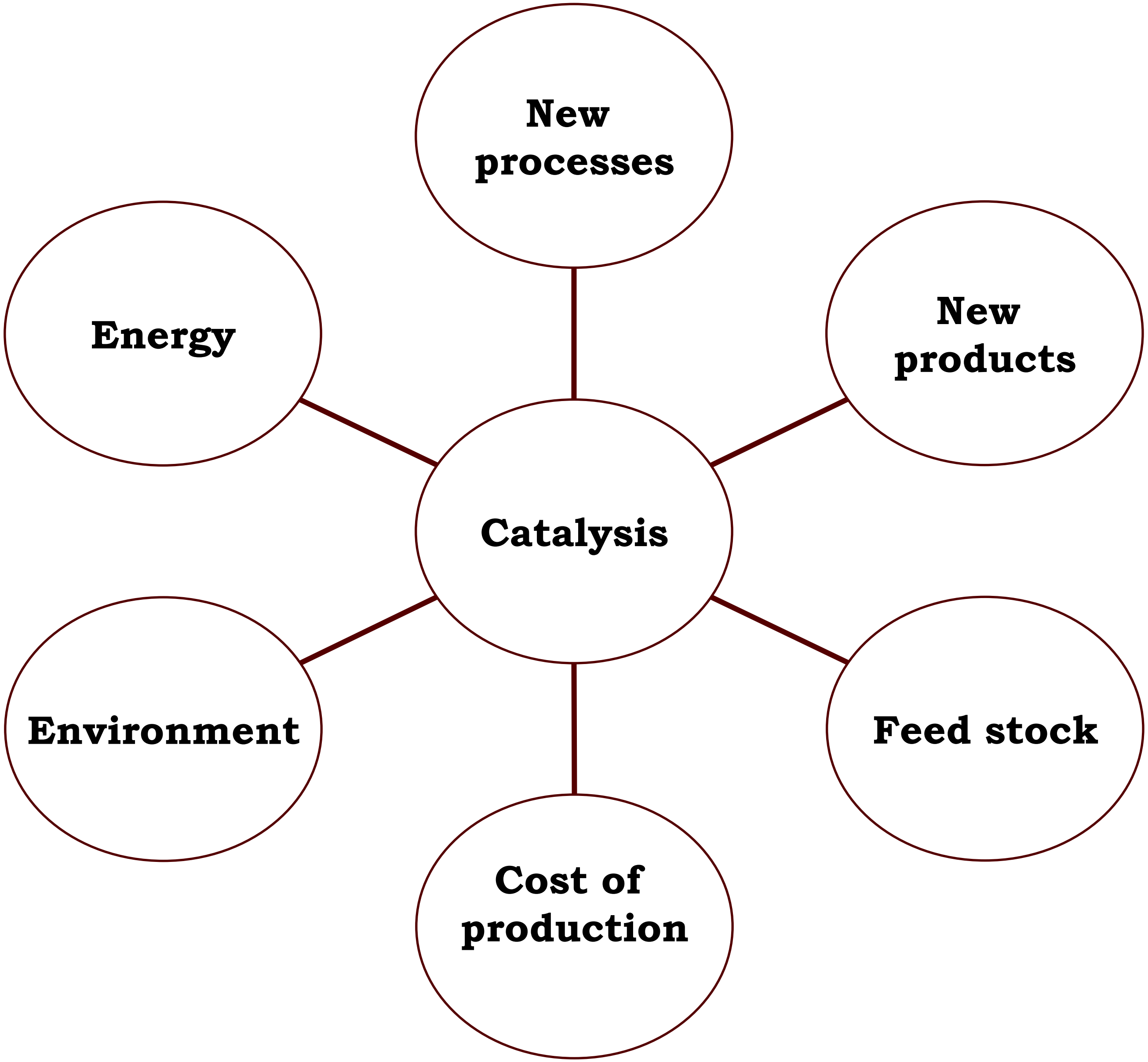
Research

Implications of catalysis

What all can a catalyst do?

- Lowering of activation energy
- Stabilization of a reactive transition state
- Bringing reactants together – proximity effect

Role of catalysis in industry



New processes

Energy

New products

Catalysis

Environment

Feed stock

Cost of production

A catalyst can help in

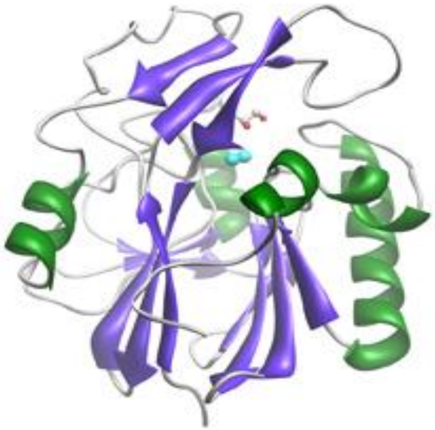
1. Efficient utilisation of raw materials
2. Development of new materials and chemicals
3. Development of systems for environmental protection
4. Development of new sources of energy
5. Development of new processes and technologies

Catalysis can address many aspects of Green Chemistry

By Reducing

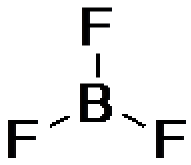
- Waste
- Materials
- Hazard
- Risk
- Energy
- Cost

Types of catalysts

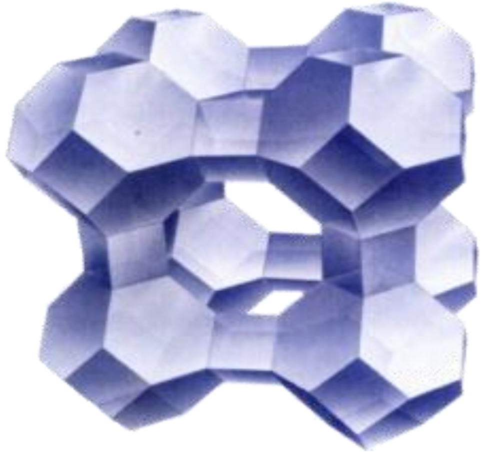


Enzyme (biocatalyst)

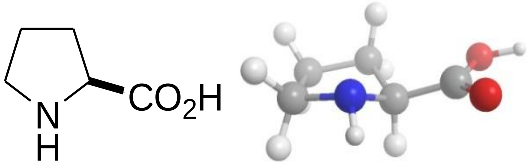
$H^{\oplus}$



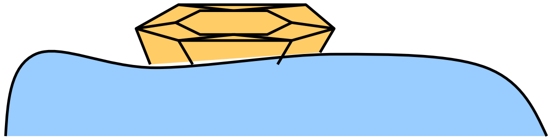
Homogeneous catalyst



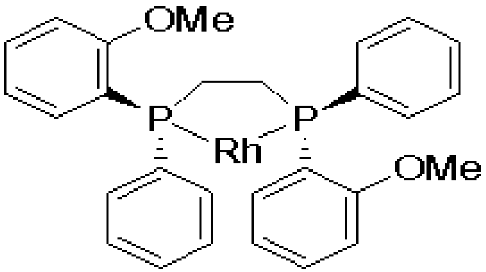
Aluminosilicate



L-proline (organocatalyst)

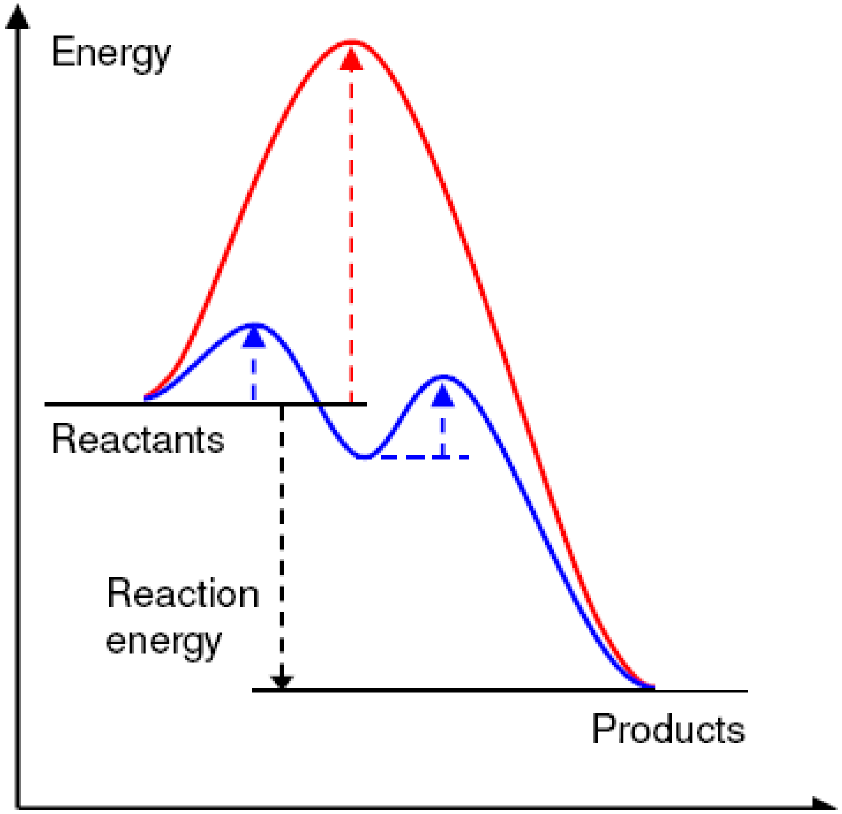


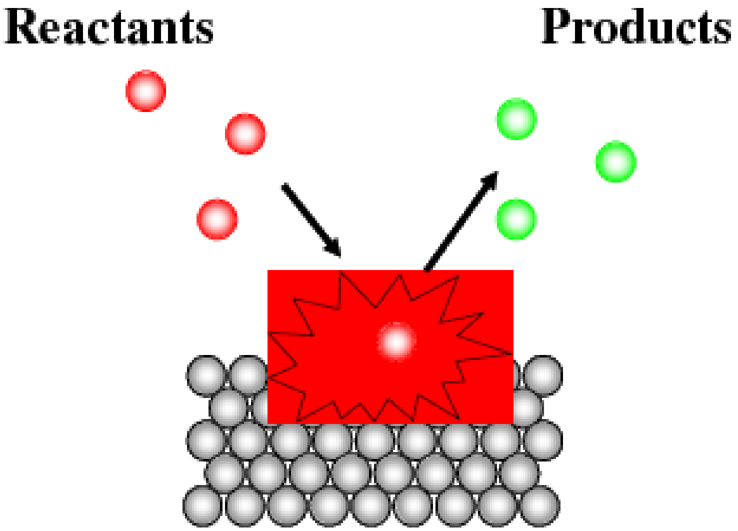
Supported catalyst

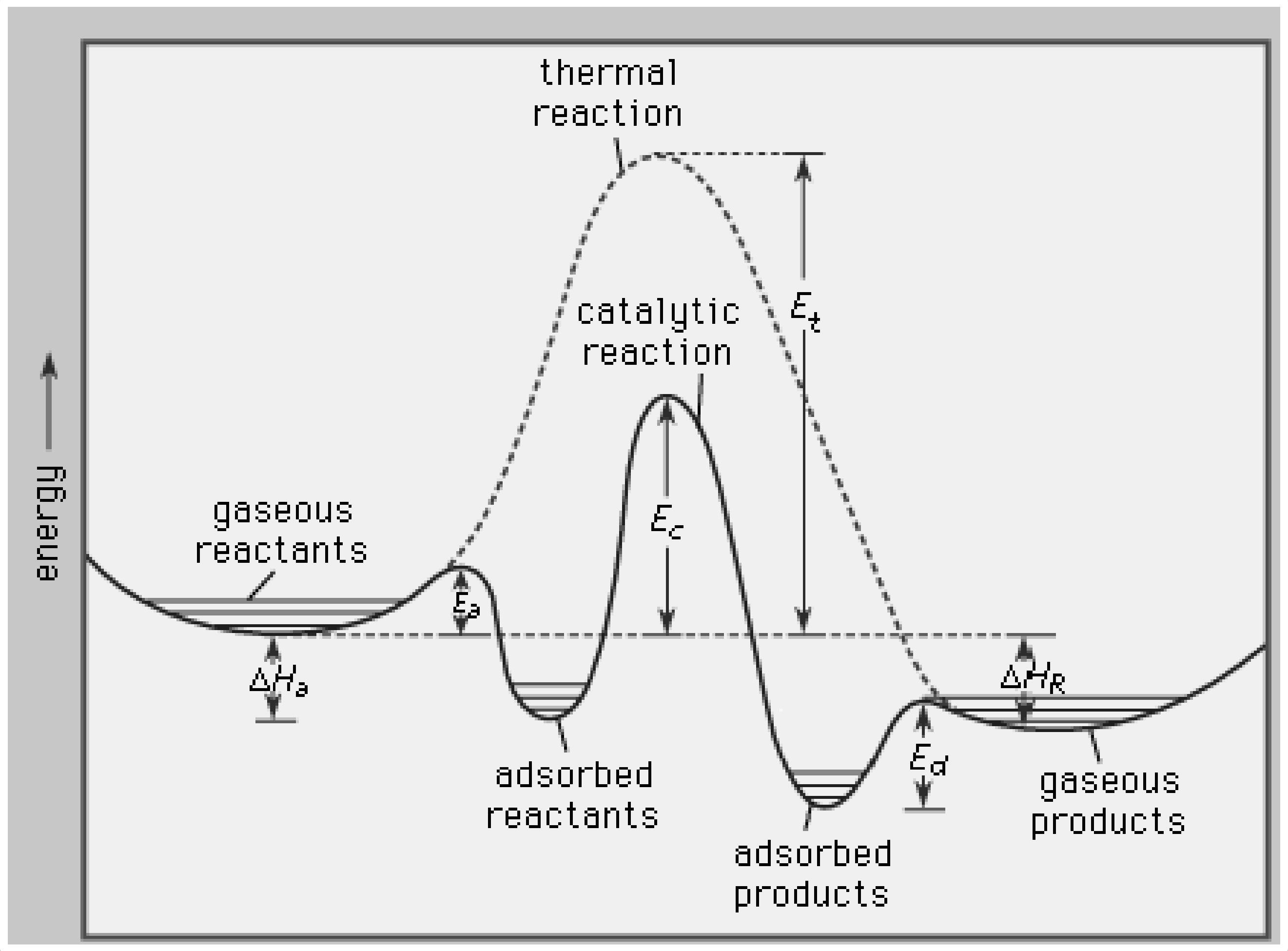


(*R*,*R*)-DiPAMP-Rh (organometallic complex)

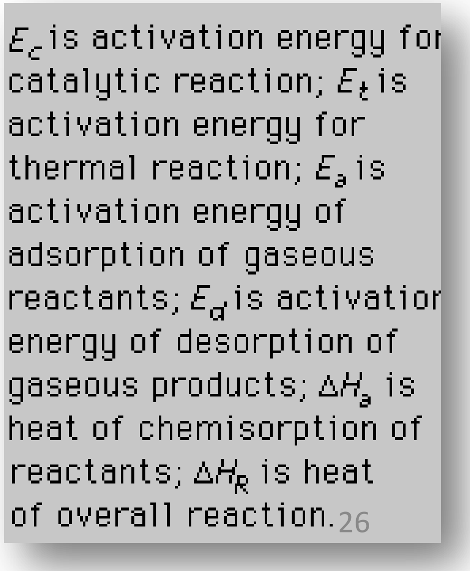
How does a catalyst work?



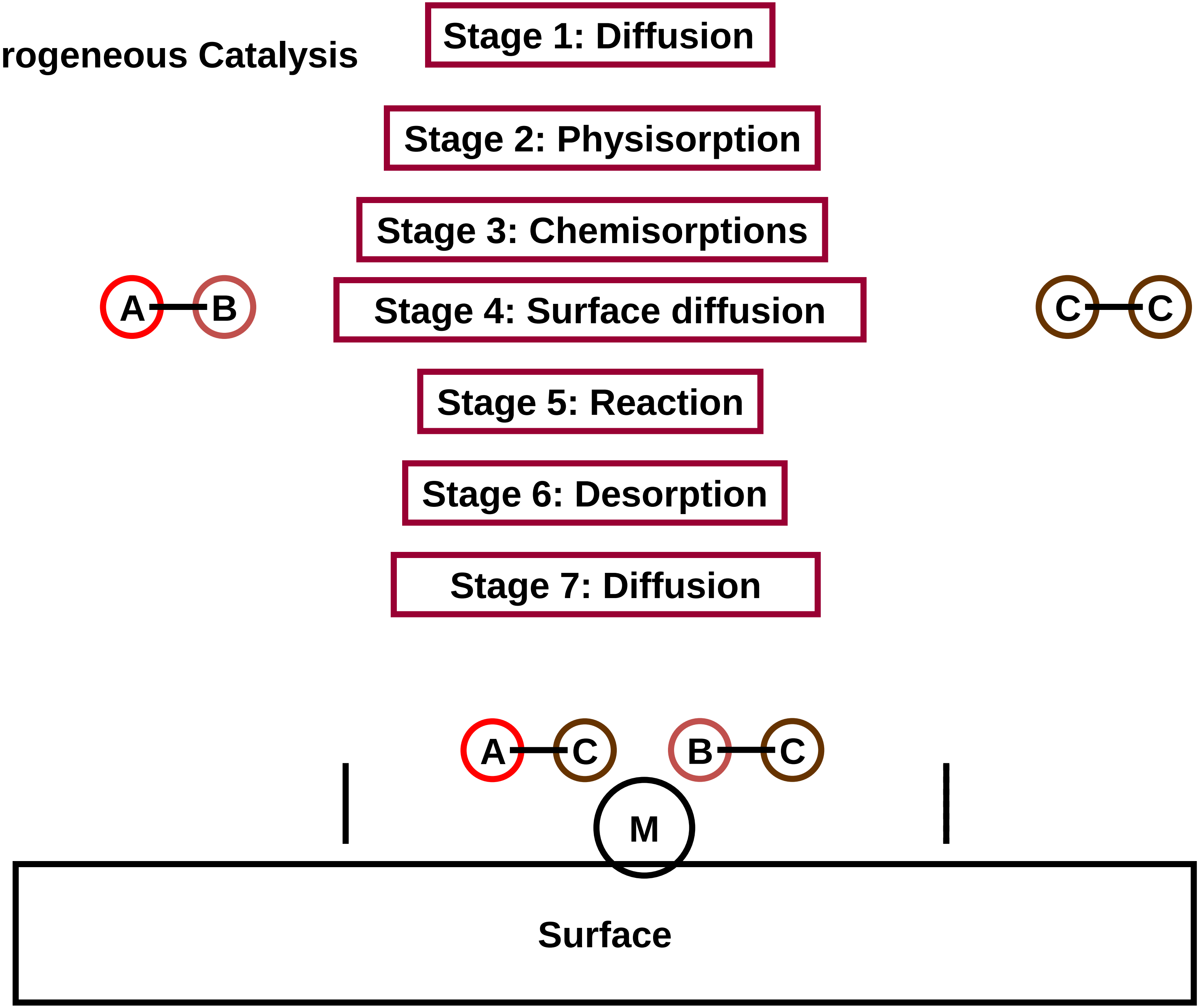




Heterogeneous Catalysis Must Always be Preceded by Adsorption


E_c is activation energy for catalytic reaction; E_t is activation energy for thermal reaction; E_a is activation energy of adsorption of gaseous reactants; E_d is activation energy of desorption of gaseous products; ΔH_a is heat of chemisorption of reactants; ΔH_R is heat of overall reaction.

Heterogeneous Catalysis



Stage 1: Diffusion

Stage 2: Physisorption

Stage 3: Chemisorptions

Stage 4: Surface diffusion

Stage 5: Reaction

Stage 6: Desorption

Stage 7: Diffusion

Heterogeneous versus Homogeneous

Heterogeneous	Homogeneous
Readily separated ✓	Difficult to separate ✗
Readily recycled / regenerated ✓	Difficult to recover ✗
Long-lived ✓	Short service life ✗
Cheap ✓	Expensive ✗
Lower rates (diffusion limited) ✗	Very high rates ✓
Sensitive to poisons ✗	Robust to poisons ✓
Lower selectivity ✗	Highly selective ✓
High energy process ✗	Mild conditions ✓
Poor mechanistic understanding ✗	Mechanisms often known ✓

Ultimate goal:
To combine the fast rates and high selectivities of homogeneous catalysts with the ease of recovery/recycle of heterogeneous catalysts

A catalyst is an antidote for -

STOICHIOMETRIC BRONSTED ACIDS & BASES

-**Aro**matic nitration - H_2SO_4 / HNO_3
Acid promoted rearrangements, e.g. Beckmann (H_2SO_4)
Base promoted condensations, e.g. Aldol (NaOH, NaOMe)

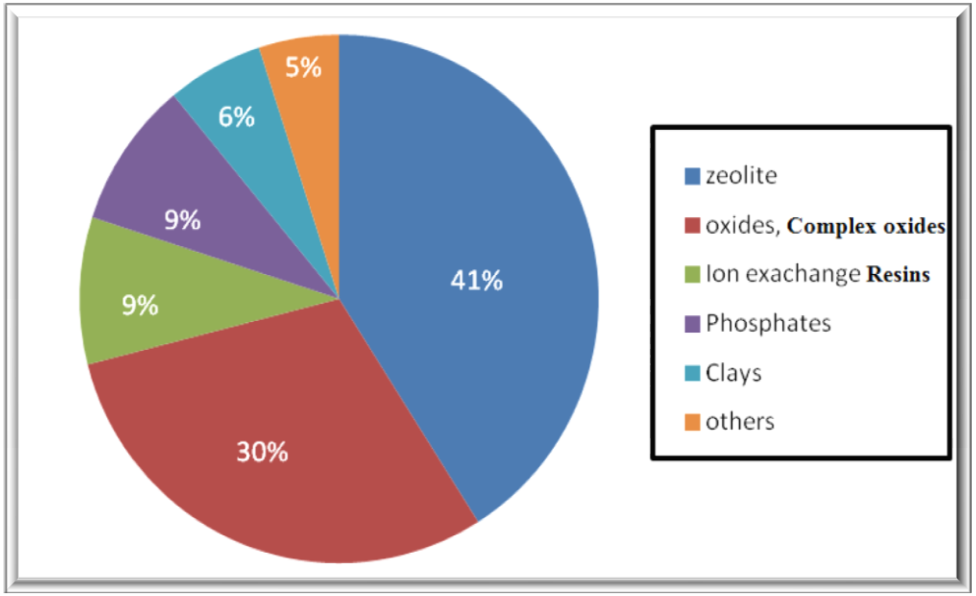
STOICHIOMETRIC LEWIS ACIDS

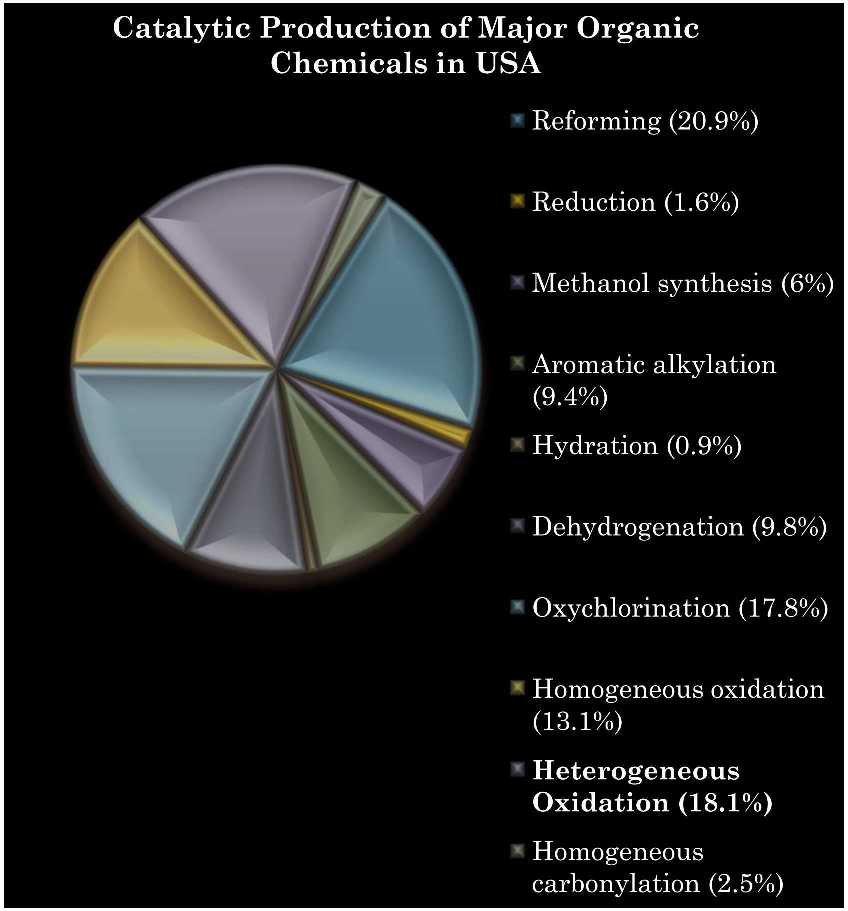
-Friedel-Crafts acylation ($AlCl_3$, $ZnCl_2$, BF_3)

STOICHIOMETRIC OXIDANTS & REDUCTANTS

- $Na_2Cr_2O_7$, $KMnO_4$, MnO_2
- $LiAlH_4$, $NaBH_4$, Zn, Fe/ HCl

Industrially important Heterogeneous Catalysts

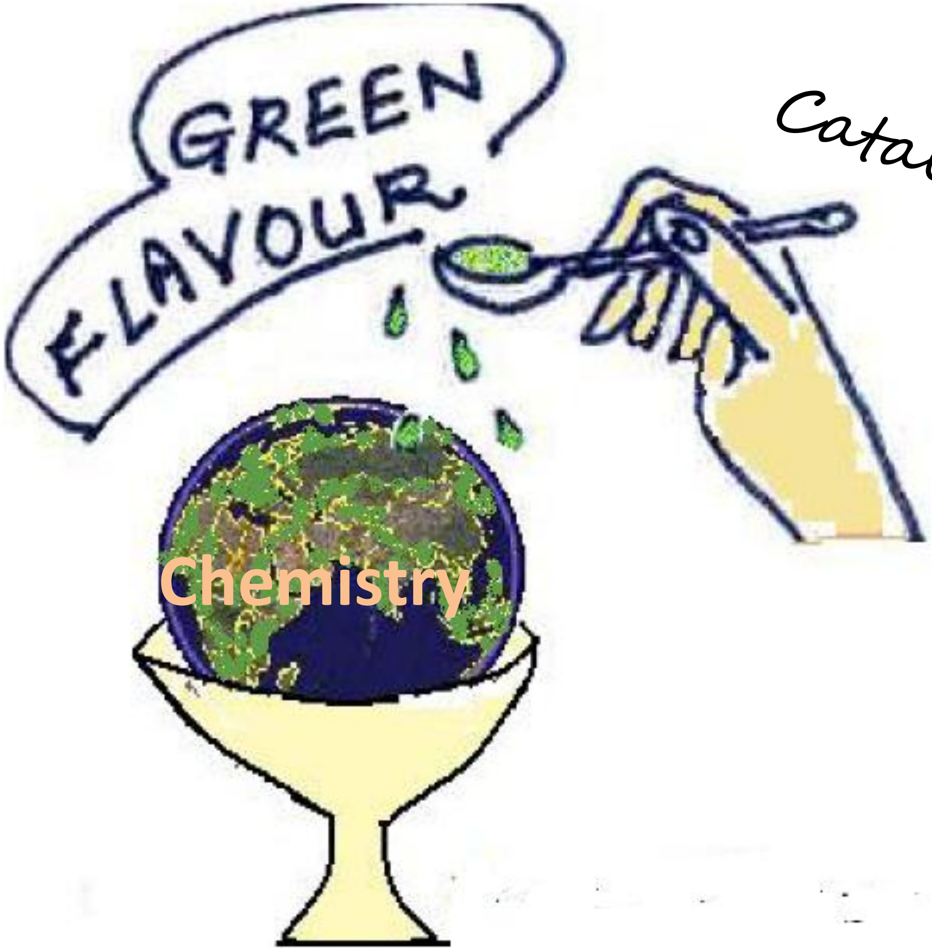




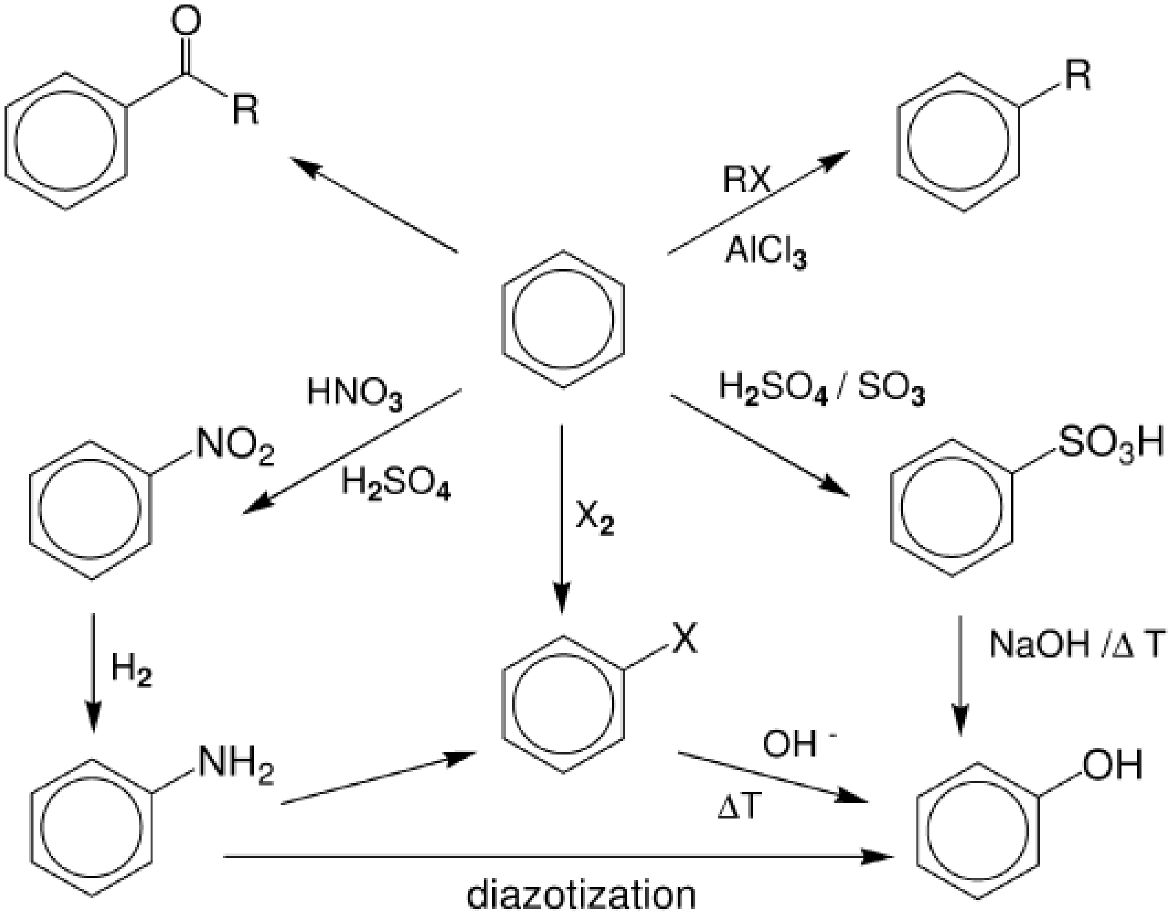
Catalysis in the Chemical Industry

- Hydrogen Industry (coal,NH_3,methanol, FT synthesis, hydrogenations, fuel cell)
- Natural gas processing
- Petroleum refining
- Petrochemicals
- Fine Chemicals (pharmaceuticals, agrochemicals, fragrance, textile, coating, surfactants)
- Environmental Catalysis

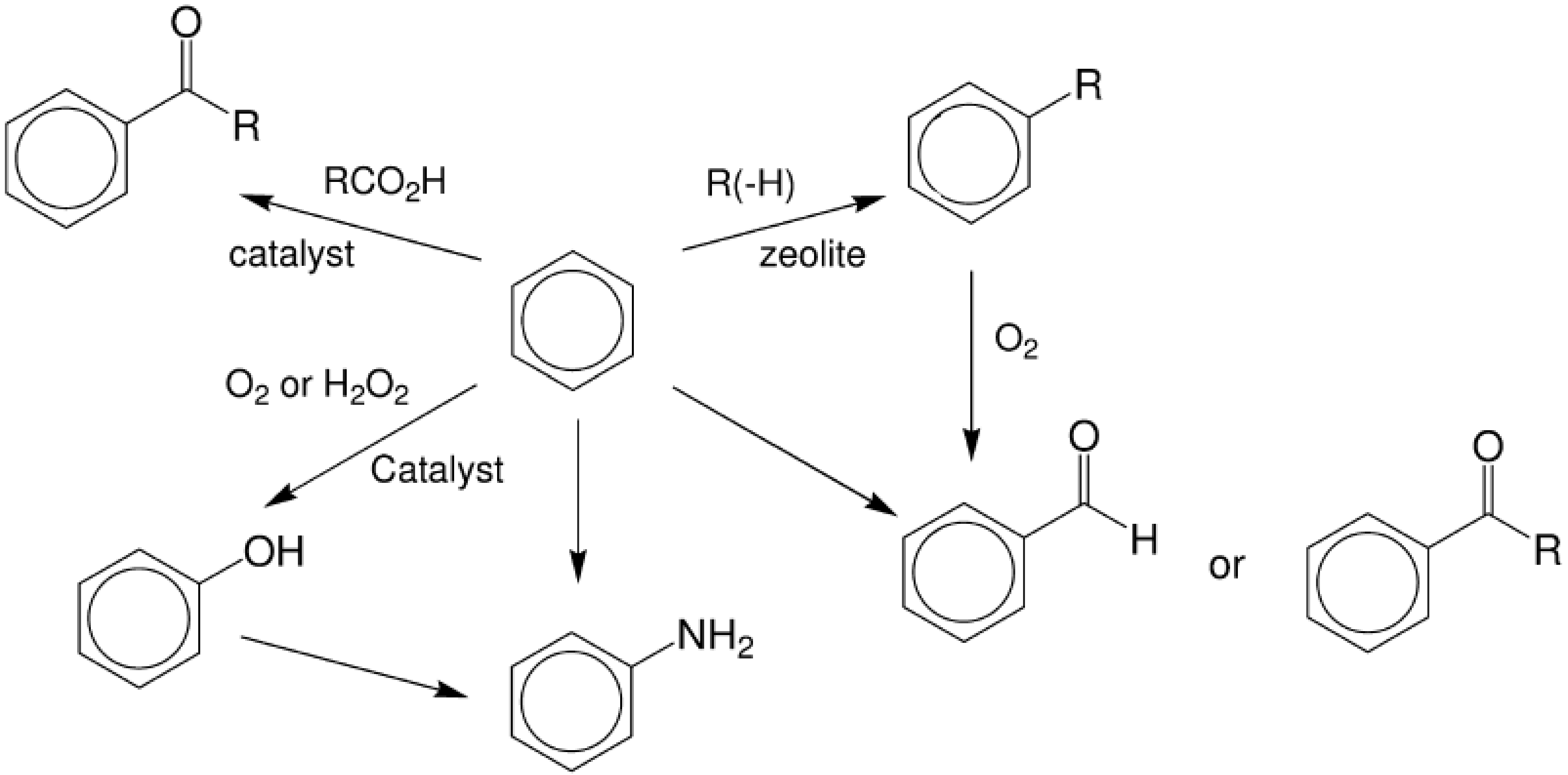
Catalysis adds



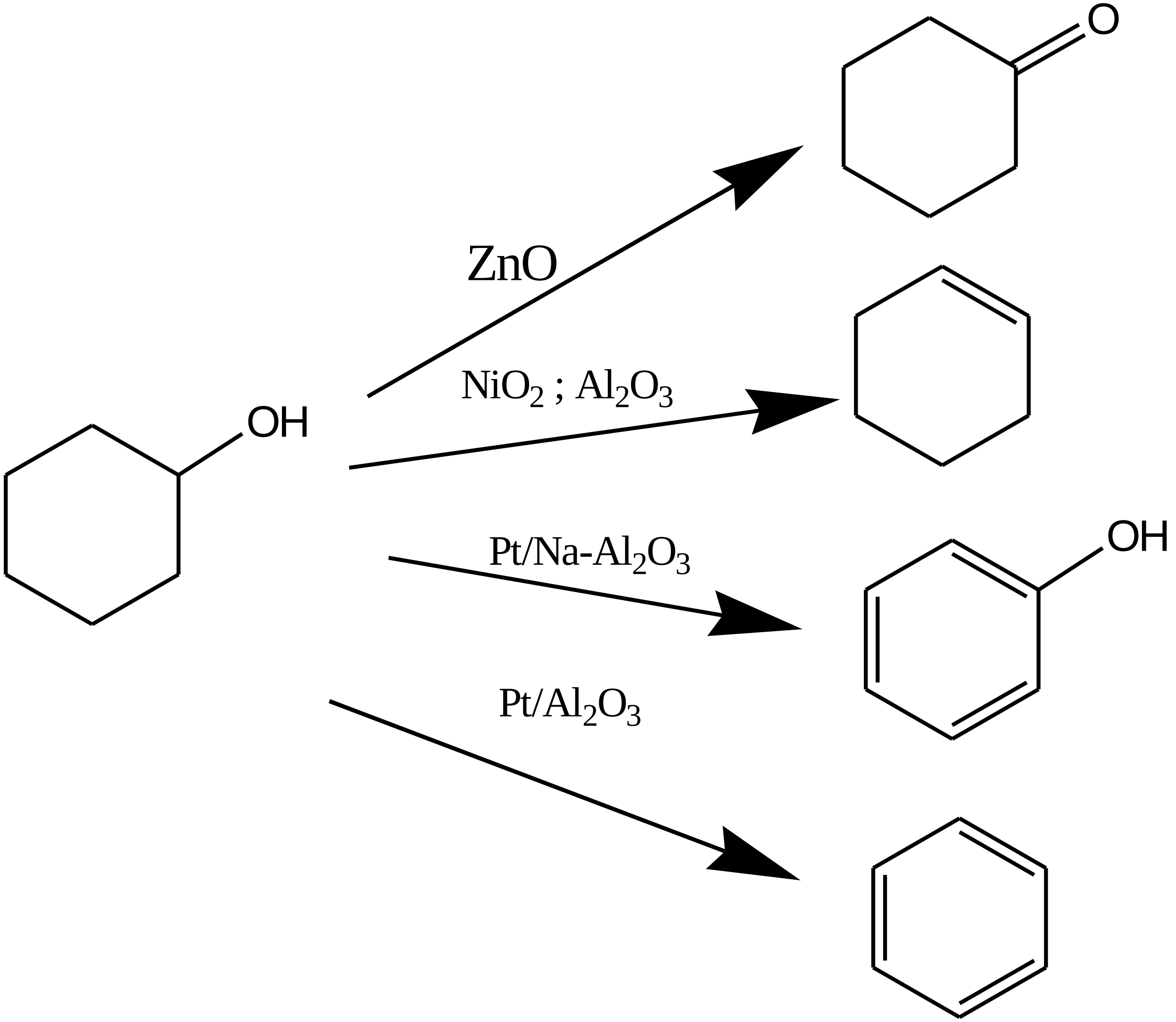
Classical Aromatic Chemistry



Green Aromatic Chemistry



Chemoselectivity



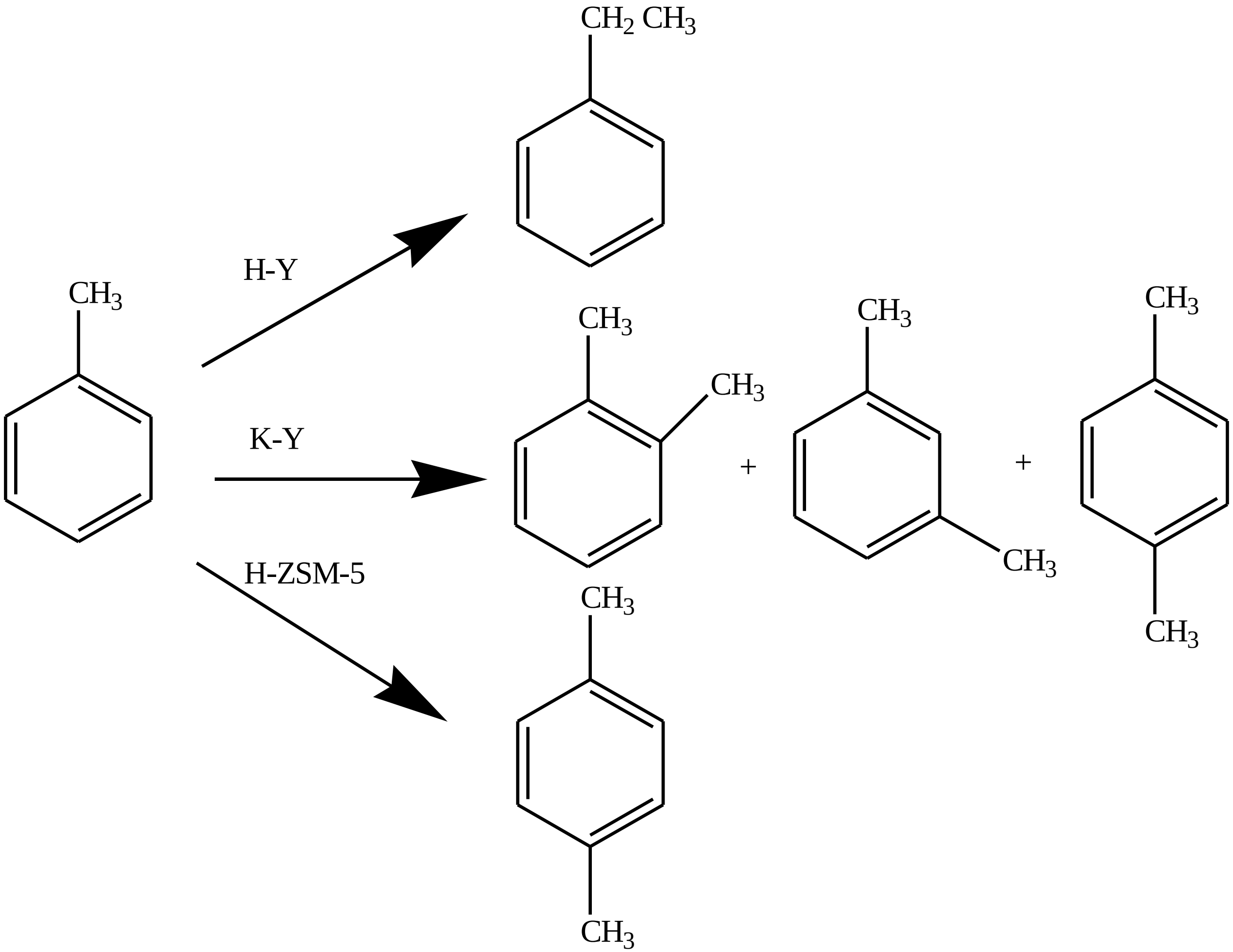
ZnO

NiO_2 ; Al_2O_3

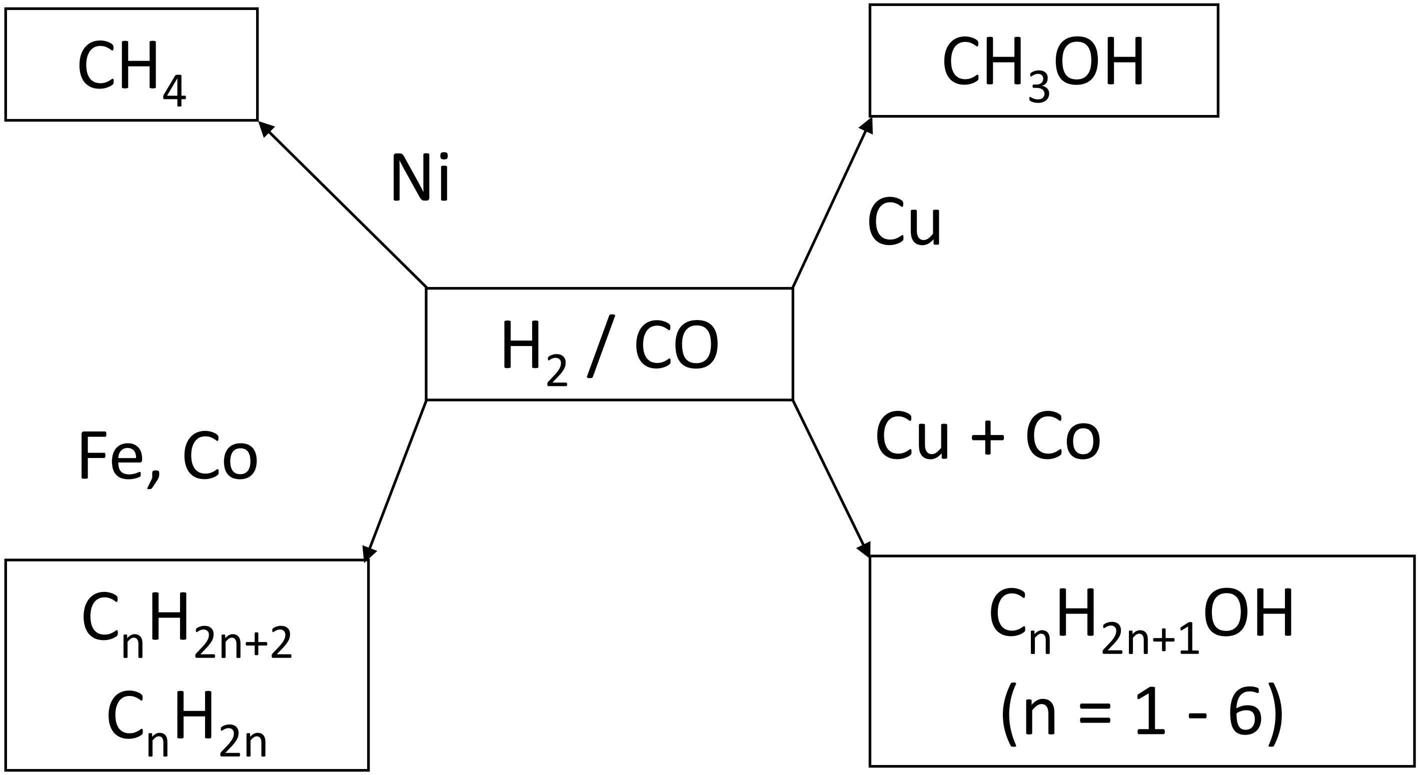
Pt/Na-Al_2O_3

Pt/Al_2O_3

Regio-selectivity



An amazing outcome form two simple molecules



H_2 / CO

Ni

CH_4

Cu

CH_3OH

Fe, Co

C_nH_{2n+2}

C_nH_{2n}

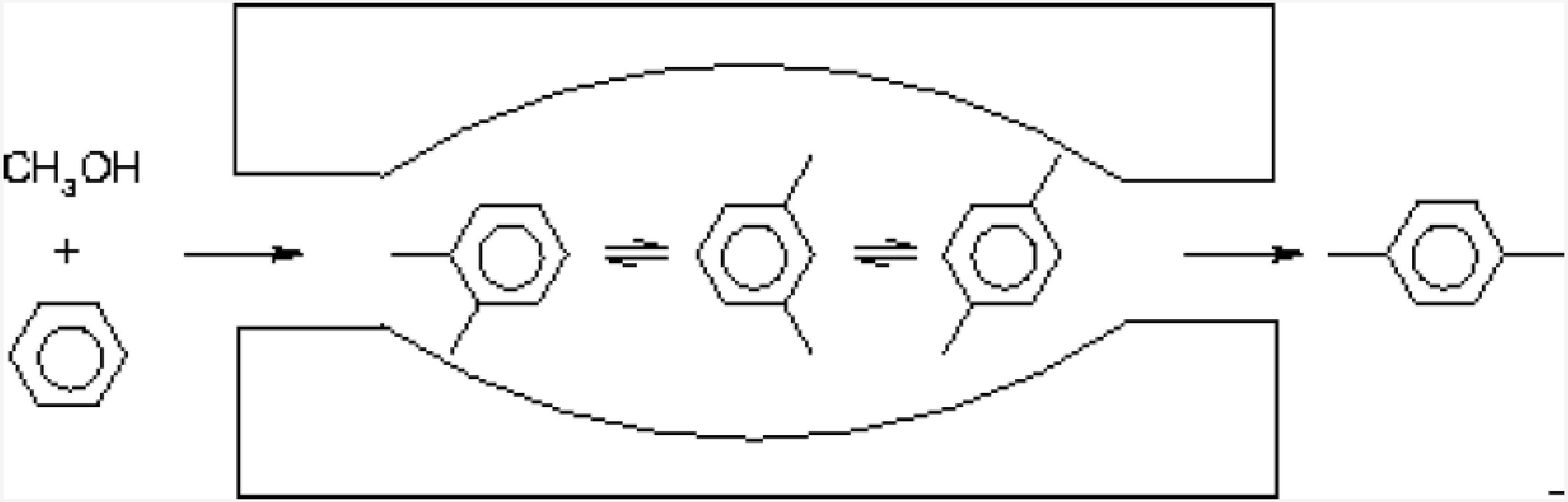
Cu + Co

$C_nH_{2n+1}OH$

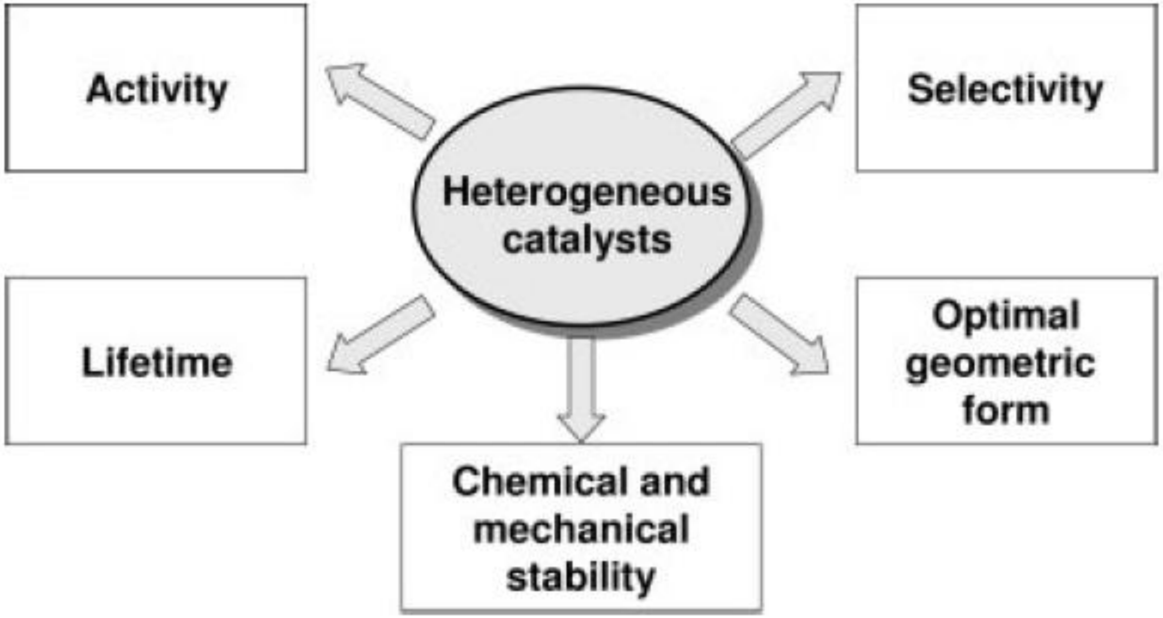
(n = 1 - 6)

Product shape Selectivity

selective diffusion of *para*-xylene out of the pores of silicalite



Performance parameters for industrial catalysts



Heterogeneous catalysis can make

hazardous processes GREEN

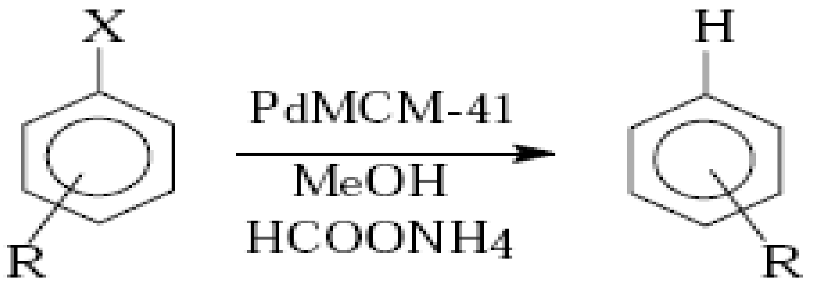
Catalytic Transfer Hydrogenation

$$\text{D-H} + \text{A} \xrightarrow{\text{Catalyst}} \text{D} + \text{A-H}$$

D-H - hydrogen donor
A - hydrogen acceptor

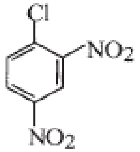
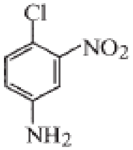
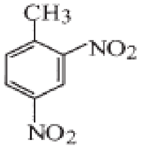
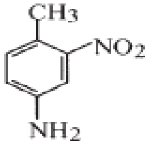
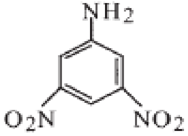
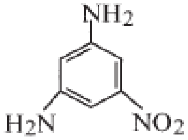
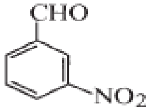
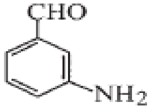
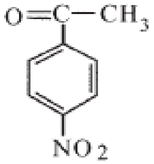
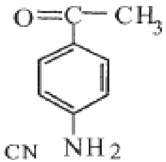
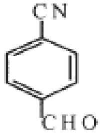
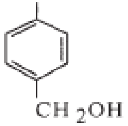
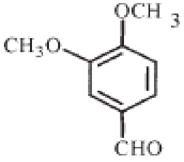
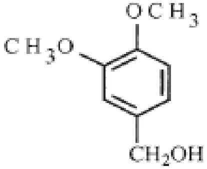
Catalytic reduction using molecular hydrogen-
high diffusibility and high flammability and high pressure present considerable hazard.
This hazard is eliminated in transfer hydrogenation process.

Reduction of nitroarenes and reductive cleavage of azo compounds via catalytic transfer hydrogenation



[X=Cl, Br, I], [R=H, NH_2, CH_3, CHO]

P.selvam, S.K.Mohapatra, S.U.Sonavane, R.V.Jayaram
Applied catalysis B: Environmental 49 (2004) 251-55

1		2.5		82	81
2		3.5		74	74
3		5.0		83	83
4		3.5		83	83
5		3.0		80	80
6		5.0		77	76
7		6.0		62	60

[a] Reaction conditions: 100 mg catalyst, 20 mmol substrate, 20 mmol KOH, 20 ml propan-2-ol, 356 K; [b] Yield = [Conversion × Selectivity] / 100.

Catalysis by solid acids and bases

Conventional acid catalyzed processes

- Advantages

  - **little technical risk**

  - high yield and product quality

- Drawbacks

  - **corrosiveness and toxicity of catalysts**

  - safety problems

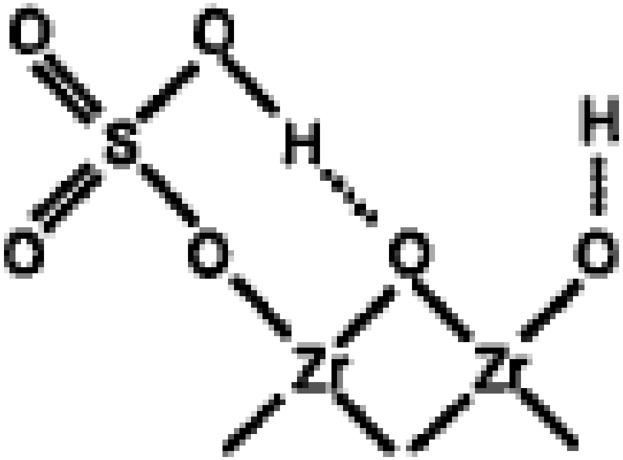
  - environmental impacts

Solid acid catalysts

- Advantages
  - **inherently safe**
  - **environmental friendly nature**
  - **low catalyst consumption**

- Drawbacks
  - **rapid deactivation**
  - **regeneration difficulties**

Surface modified metal oxides as solid acid catalysts



Preparation of surface modified metal oxides

0.25 M solution of zirconium oxychloride

Aqueous ammonia soln. (drop wise addition) RT (30 ^{0}C)
pH = 8.0

Zirconium Hydroxide

Air dried at 100° C for 24 h, added dropwise acidic aqueous soln

of sulphuric acid

Air dried at 120° C for 24 h
calcined at 500° C for 2 h

SO_4^{2-}/ZrO_2

Method can be extended to SO_4^{2-}/Fe_2O_3, SO_4^{2-}/CeO_2, SO_4^{2-}/TiO_2

BET surface area and total acidity

Catalyst	BET Surface area ($m^2.g^{-1}$)	Total acidity ($mmol . g^{-1}$)[a]
$SO_4^{2-}/Ce_{0.02}Zr_{0.98}O_2$	22	3.17
$SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$	52	4.23
$SO_4^{2-}/Ce_{0.10}Zr_{0.90}O_2$	28	3.52
$SO_4^{2-}/Ce_{0.15}Zr_{0.85}O_2$	14	3.50

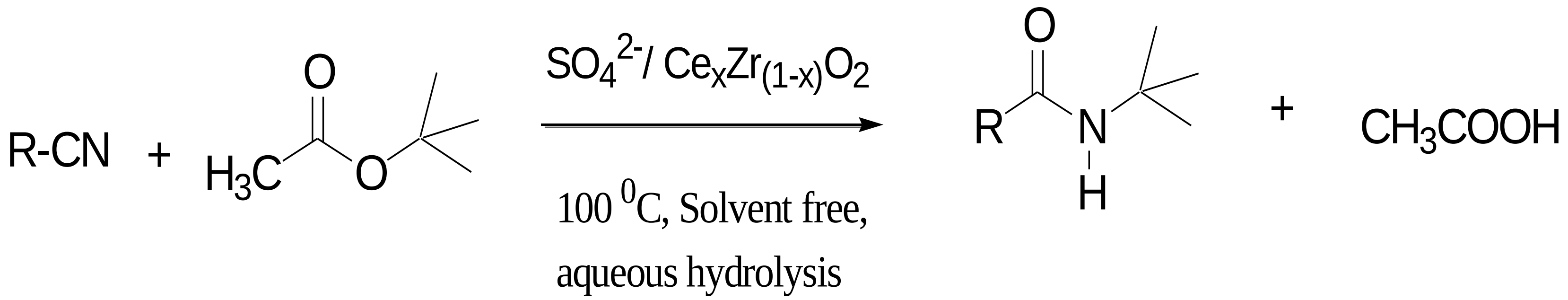
[a] All the catalysts were calcined at 650 ºC

BET surface area and total acidity

Catalyst	BET Surface area ($m^2.g^{-1}$)	Total acidity (mmol $.g^{-1}$)
$SO_4^{2-}/Y_{0.04}Zr_{0.96}O_2$	32	1.23
$SO_4^{2-}/Y_{0.08}Zr_{0.92}O_2$	43	1.64
$SO_4^{2-}/Y_{0.12}Zr_{0.88}O_2$	52	1.93
$SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$	75	4.19
$SO_4^{2-}/Y_{0.24}Zr_{0.76}O_2$	29	2.65

All the catalysts were calcined at 500 ^{0}C

$SO_4^{2-}/Ce_xZr_{1-x}O_2$ catalyzed modified Ritter reaction using tert-butyl acetate with nitriles



R= alkyl,aryl

Sandeep S. Kahandal, Sandip R. Kale, Shamrao T. Disale and Radha V. Jayaram, ***Chemistry Letters*** *: 2012,41, 7, 738*;

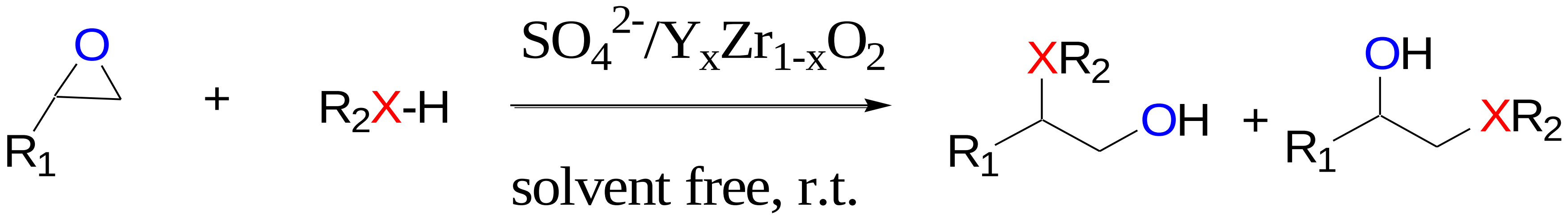
Sandeep S. Kahandal, Sandip R. Kale, Shamrao T. Disale and Radha V. Jayaram
Synfacts 2012, 8,10,1161

Amidation of *tert*-butyl acetate with benzonitrile

Entry	Catalyst	E_i (mV)[b]	Total acidity (mmol g^{-1})[c]	Yield (%)[d]	Initial rate (mmol h^{-1} gm^{-1}) x 10^3
1	-	--	--	N.R.[e]	-
2	CeO_2	27	0.3	N.R.[e]	-
3	ZrO_2	55	0.8	17	0.38
4	SO_4^{2-}/CeO_2	154	1.22	19	0.51
5	SO_4^{2-}/ZrO_2	168	2.07	27	0.95
6	$SO_4^{2-}/Ce_{0.02}Zr_{0.98}O_2$	440	3.17	54	1.05
7	**$SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$**	**560**	**4.23**	**78**	**1.65**
8	$SO_4^{2-}/Ce_{0.10}Zr_{0.90}O_2$	450	3.52	64	1.38
9	$SO_4^{2-}/Ce_{0.15}Zr_{0.85}O_2$	440	3.50	58	1.25
10	$SO_4^{2-}/Ce_{0.17}Zr_{0.83}O_2$	360	2.75	45	1.13
11	$SO_4^{2-}/Ce_{0.20}Zr_{0.80}O_2$	295	2.01	31	0.92
12	$SO_4^{2-}/Y_{0.04}Zr_{0.96}O_2$	148	1.23	18	0.60
13	$SO_4^{2-}/Y_{0.08}Zr_{0.92}O_2$	195	1.64	23	0.87
14	$SO_4^{2-}/Y_{0.12}Zr_{0.88}O_2$	310	1.93	25	0.97
15	$SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$	530	4.19	65	1.25
16	$SO_4^{2-}/Y_{0.20}Zr_{0.80}O_2$	330	2.91	45	1.42
17	$SO_4^{2-}/Y_{0.24}Zr_{0.76}O_2$	248	2.65	37	0.98
18	$SO_4^{2-}/CeO_2 + SO_4^{2-}/ZrO_2$	-	-	39	0.81

[a]Reaction conditions: benzonitrile (2 mmol), *tert*-butyl acetate (4 mmol), catalyst (20 wt%) , solvent free, 5 h., 100 °C [b]E_i- Inital electrode potential (mV),[c] Total acidity values determined by n-butylamine potentiometric titration method, [e] No reaction, [d] Isolated yield,

II. Regioselective epoxide ring opening by alcohols



(A) (B)

R_1 = alkyl, aryl
R_2 = alkyl,aryl
X = O,N

S. S. Kahandal , S. R. Kale and R. V. Jayaram, ***Catalysis Science and Technology*** 2012, 2, 1493–1499

Synthesis of β-alkoxy alcohols on solid acids

Entry	Catalyst	Time	Acidity (mmol /g)[c]	E_i (mV)[d]	Initial rate (mmol h $^{-1}$ g^{-1}) x 10 ^{4}	Yield[b] (%)
1	-	5	-	-	-	-
2	ZrO_2	5	0.81	55	-	-
3	SO_4^{2-}/ZrO_2	0.5	2.07	168	2.21	59
4	Y_2O_3- ZrO_2	0.5	0.90	91	1.18	35
5	$SO_4^{2-}/Y_{0.04}Zr_{0.96}O_2$	0.5	1.23	148	1.37	42
6	$SO_4^{2-}/Y_{0.08}Zr_{0.92}O_2$	0.5	1.64	195	2.06	64
7	$SO_4^{2-}/Y_{0.12}Zr_{0.88}O_2$	0.5	1.93	310	4.57	83
8	**$SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$**	**0.5**	**4.19**	**530**	**7.0**	**96**
9	$SO_4^{2-}/Y_{0.20}Zr_{0.80}O_2$	0.5	2.91	330	4.62	79
10	$SO_4^{2-}/Y_{0.24}Zr_{0.76}O_2$	0.5	2.65	248	1.20	52
11	$SO_4^{2-}/Ce_{0.02}Zr_{0.98}O_2$	0.5	3.17	440	2.22	65
12	$SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$	0.5	4.23	560	4.98	87
13	$SO_4^{2-}/Ce_{0.10}Zr_{0.90}O_2$	0.5	3.52	450	3.57	74
14	$SO_4^{2-}/Ce_{0.15}Zr_{0.85}O_2$	0.5	3.50	460	2.82	69

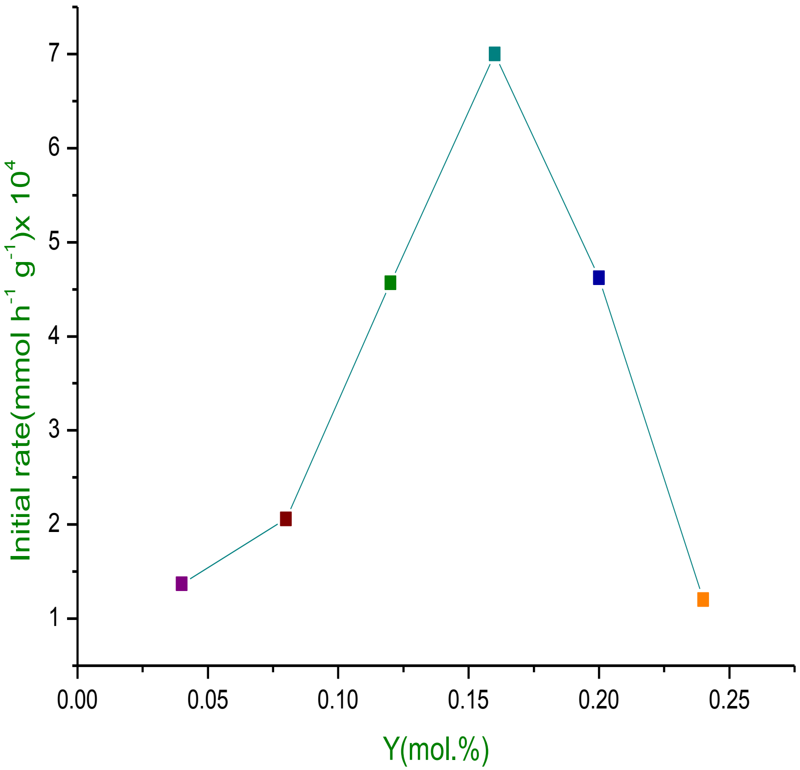
[a] [a]Reaction conditions: styrene oxide (2 mmol), ethanol (2 mmol) , solvent free, r.t (32 ºC), [b]E_i- Inital electrode potential (mV),

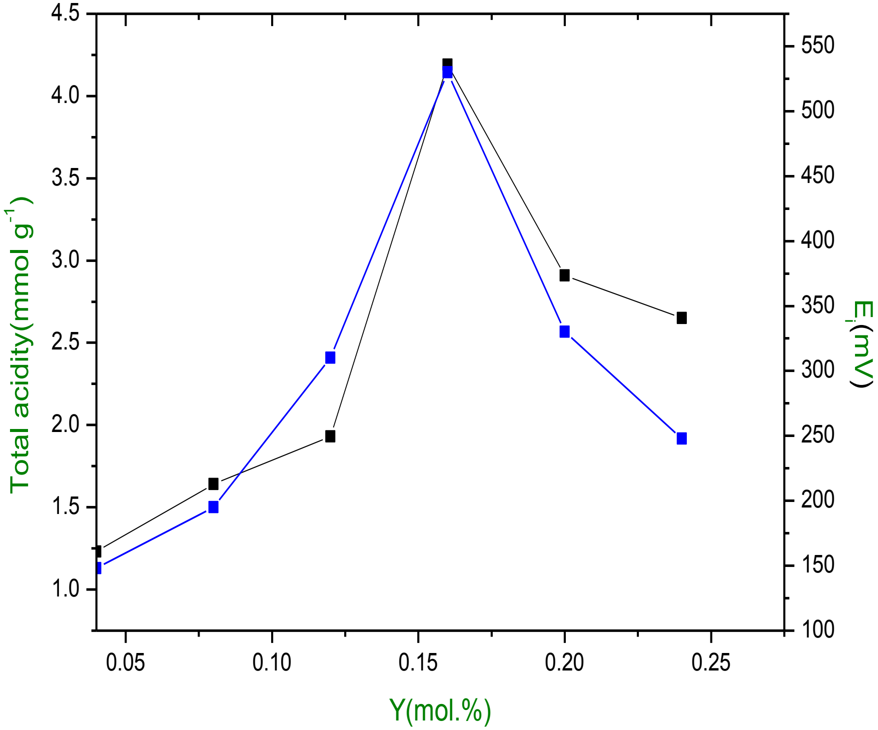
[c] Total acidity values determined by n-butylamine potentiometric titration method,

[b] GC Yield

Mol.% of Y in SO_4^{2-}/ $Y_x Zr_{(1-x)}O_2$ (x = 0.04-0.24) Vs V_0

Total acidity (mmol g^{-1}) and initial electrode potential (mV) with $SO_4^{2-}/Y_xZr_{1-x}O_2$ (x= 0.04-0.24)





Catalysis by solid bases

- There is a great demand for solid base catalysts uti in chemical processes.In particular, in the synthesis of fine and intermediate chemicals where E-factors are in the range 1 - 50.

- In most cases, basic sites appear on the surface as surface O atoms of metal oxides by removing H_2O and CO_2 from the surfaces.

Solid base catalysts

- **Hydrotalcites** – $[M(II)1{-}xM(III)x\ (OH)_2] \cdot A_{n-\ x/n} \cdot mH_2O$.

  [M(II): **Mg**, **Zn**, **Cu**] [M(III): **Al**]

- **Hydroxyapatites** – $M_{10}(PO_4)_6(OH)_2$

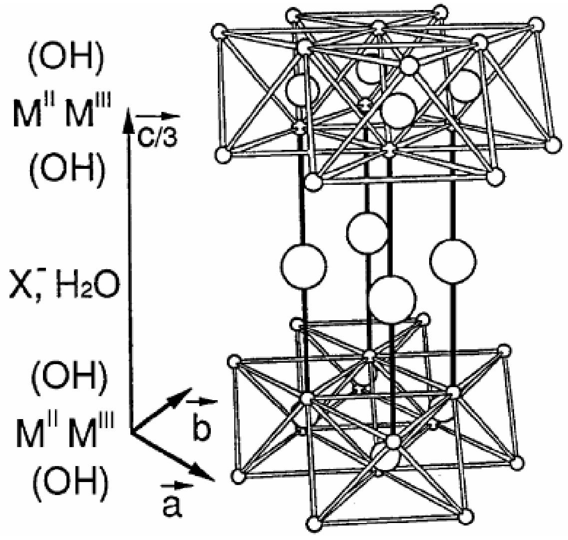
  M-HAP (M= **Zn**, **Cu**, **Pd**)

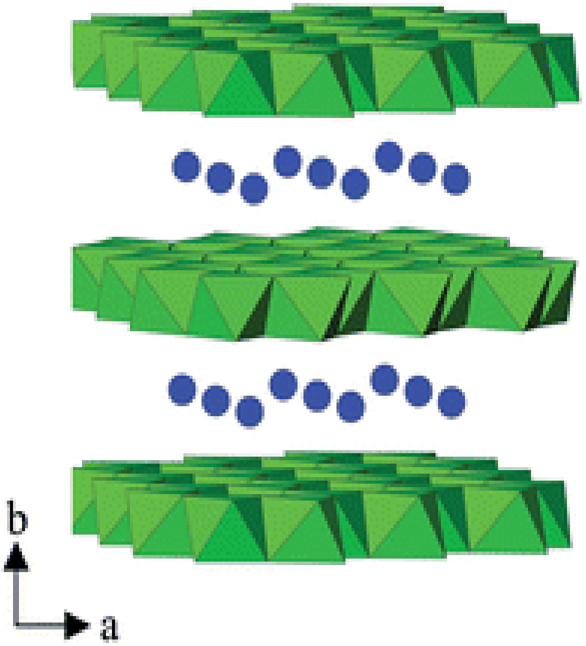
  M-FAP (M= **Cu**)

  M-CAP (M= **Cu**)

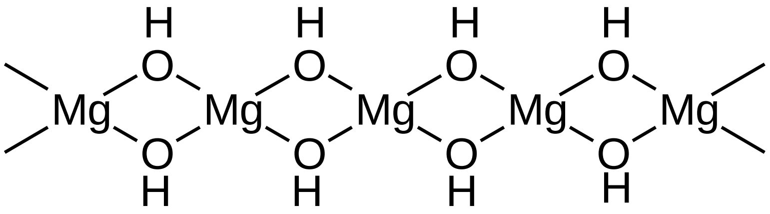
  γ-Fe_2O_3/HAP

Structure of Hydrotalcite





$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n}).zH_2O$$



Brucite-$Mg(OH)_2$

Basicity measurement by phenol adsorption

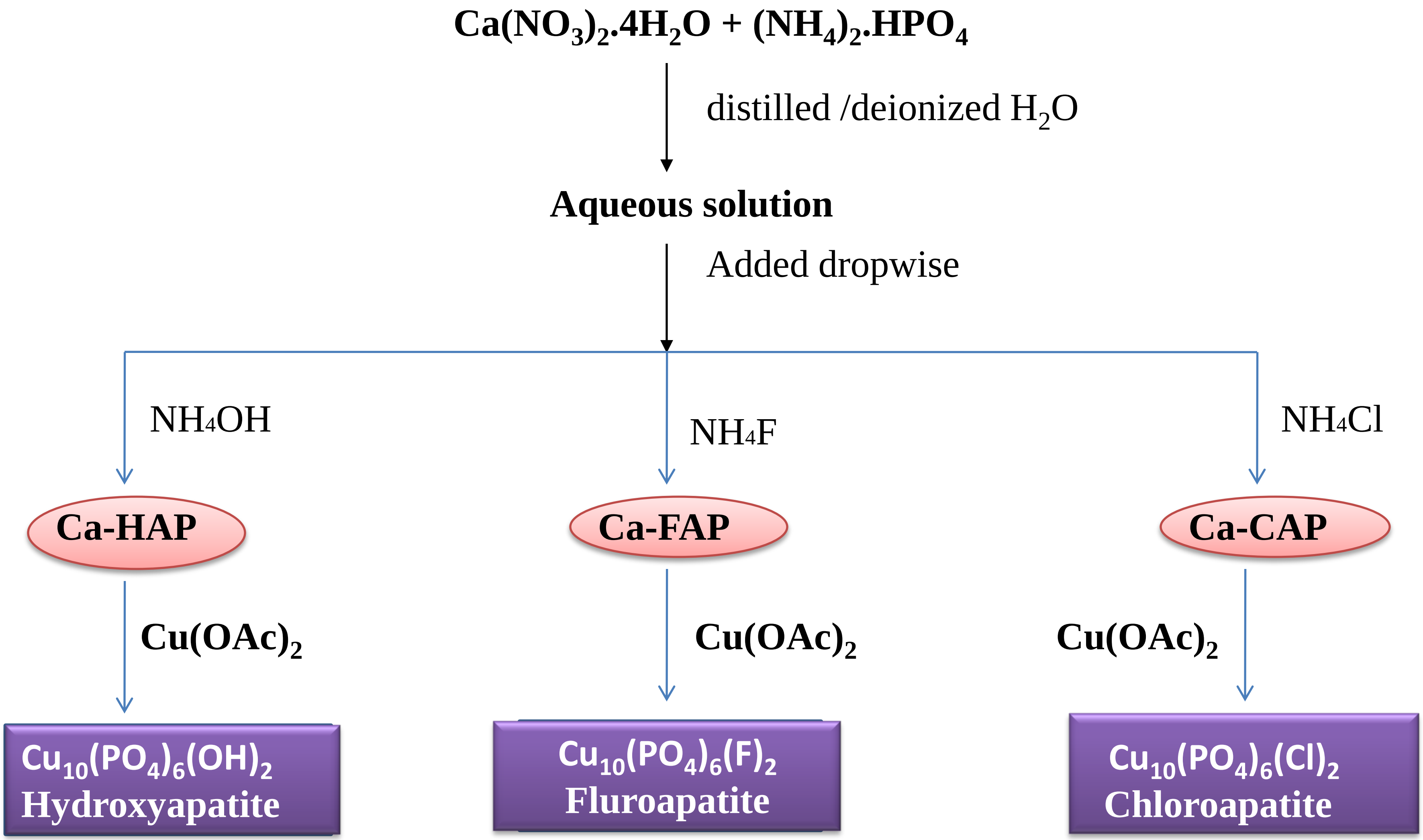
$$q_e = \frac{(Co\text{-}Ce) \times V}{W}$$

qe – quantity of phenol adsorbed
C - initial conc. of phenol
Ce- conc. of phenol at equilibrium
W- wt. of the catalyst (gm)

Hydroxyapatites

- General formula: $M_{10}(PO_4)_6(OH)_2$
- Copper Hydroxyapatite $Cu_{10}(PO_4)_6(OH)_2$
- Hydroxyapatites are the main component of bones and teeth
- Have basic property and ion exchange ability.

Preparation of Apatite catalysts



$Ca(NO_3)_2.4H_2O + (NH_4)_2.HPO_4$

distilled /deionized H_2O

Aqueous solution

Added dropwise

NH_4OH

NH_4F

NH_4Cl

Ca-HAP

Ca-FAP

Ca-CAP

$Cu(OAc)_2$

$Cu(OAc)_2$

$Cu(OAc)_2$

$Cu_{10}(PO_4)_6(OH)_2$
Hydroxyapatite

$Cu_{10}(PO_4)_6(F)_2$
Fluroapatite

$Cu_{10}(PO_4)_6(Cl)_2$
Chloroapatite

One Pot synthesis of 2-amino-4H-chromene using hydrotalcite as a solid base

R, V.Jayaram, S.Kale ,Catalysis Science & Technology,
01 August 2013, Issue 8,
Page 1857 to 2148

Characteristic features

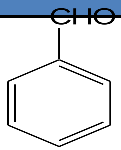
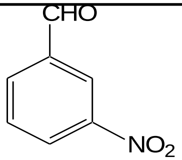
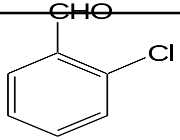
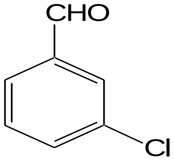
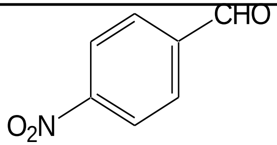
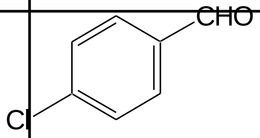
Entry	Catalyst	Surface area m^2/g	Basicity[a] (mmol/g)	Yield[b] (%)
1	Mg-Al :2.0 HT	146	0.087	65
2	Mg-Al :3.0 HT	185	0.095	72
3	Mg-Al :4.0HT	236	0.117	78
4	Mg-Al :5.0 HT	269	0.131	95

[a] Determined by Phenol adsorption method

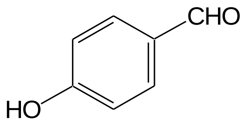
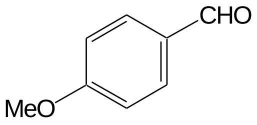
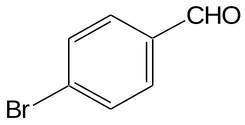
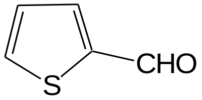
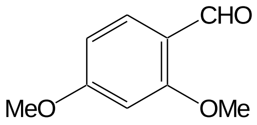
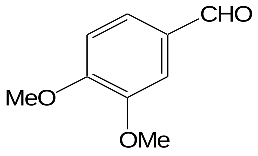
[b] Isolated Yield

HT-Hydrotalcite

Application of the method to various substrates

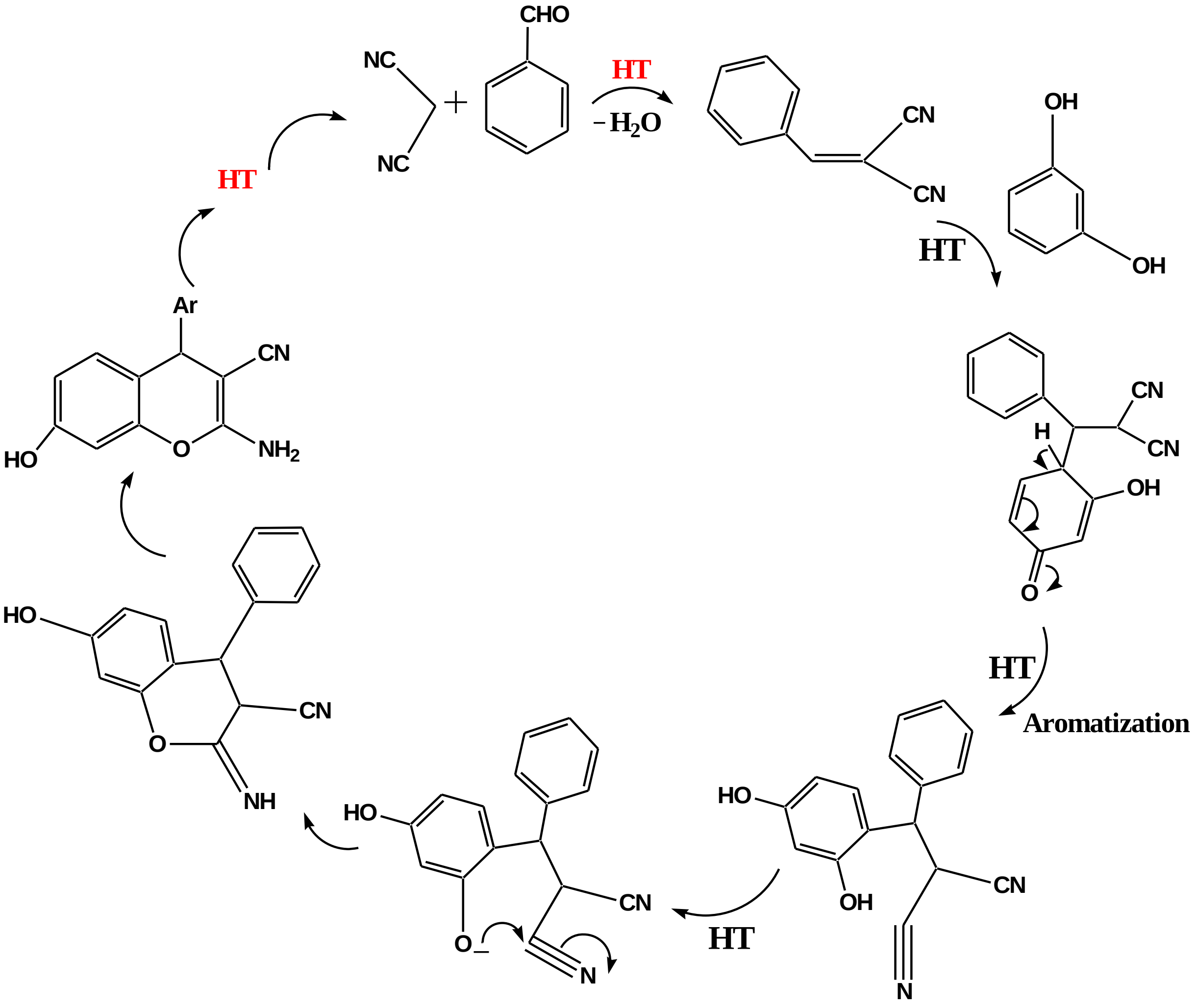
No	Aldehydes	Chromene	Time(h)	Yield [b] (%)	M.P. (Obs.)/^{0}C
1		4a	4	95	234-236
2		4b	4	92	188-192
3		4c	4.5	87	96-98
4		4d	4	95	176-178
5		4e	3	96	210-212
6		4f	5	90	160-162

[a] Reaction condition: resorcinol (3 mmol), malononitrile (3 mmol), aldehyde (3 mmol) and 15 wt% of Mg/Al HT (5:1) catalysts in 10 ml of water at 60°C.. [b] Isolated yields

Entry	Aldehydes	Chromene	Time(h)	Yieldb (%)	M.P. (Obs.)
7		4g	5.5	83	248-250
8		4h	6	79	112-114
9		4i	5	85	224-226
10		4j	4.5	90	216-218
11		4k	6	86	198-200
12		4l	6	88	214-216

[a] Reaction condition: resorcinol (3 mmol), malononitrile (3 mmol), aldehyde (3 mmol) and 15 wt% of Mg/Al HT (5:1) catalysts in 10 ml of water at 60ºC. [b] Isolated yields

Reaction Mechanism



Conclusions

- Hydrotalcite catalyzed one pot multicomponent reaction of resorcinol, malononitrile and aldehyde for the synthesis of 2-amino-4H chromene in wateras a green solvent.

- The catalyst offers advantages like reusability, ease of separation of the products and high yields of the desired products.

- Multicomponent reaction of alkyne, halide and sodium azide catalyzed by copper apatite as a heterogeneous base catalyst in water.

Sandip R. Kale, Sandeep S. Kahandal, Shamrao T. Disale and Radha V.
Jayaram* *Current Chemistry Letter, 2012, 1, 47-58.*

Bifunctional catalysis

What is a bifunctional catalyst ?

- Catalysts having more than one type of active sites which are capable of catalyzing more than one type of reaction

- These active sites can participate either in simultaneous or sequential reactions.

- Reduce the number of process steps.

Types of bifunctional catalysts

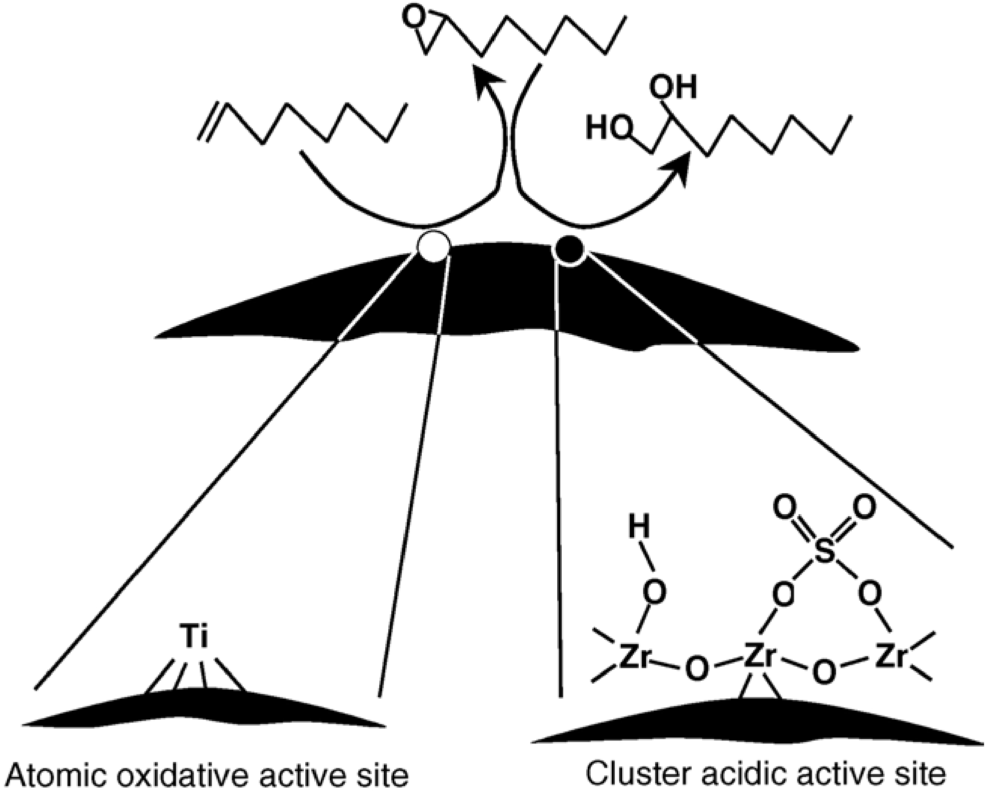
- Acid-Base
- Acid-Oxidation
- Acid-Reduction

- Base-Oxidation
- Base-Reduction
- Oxidation-Reduction

Recently used bifunctional catalysts-

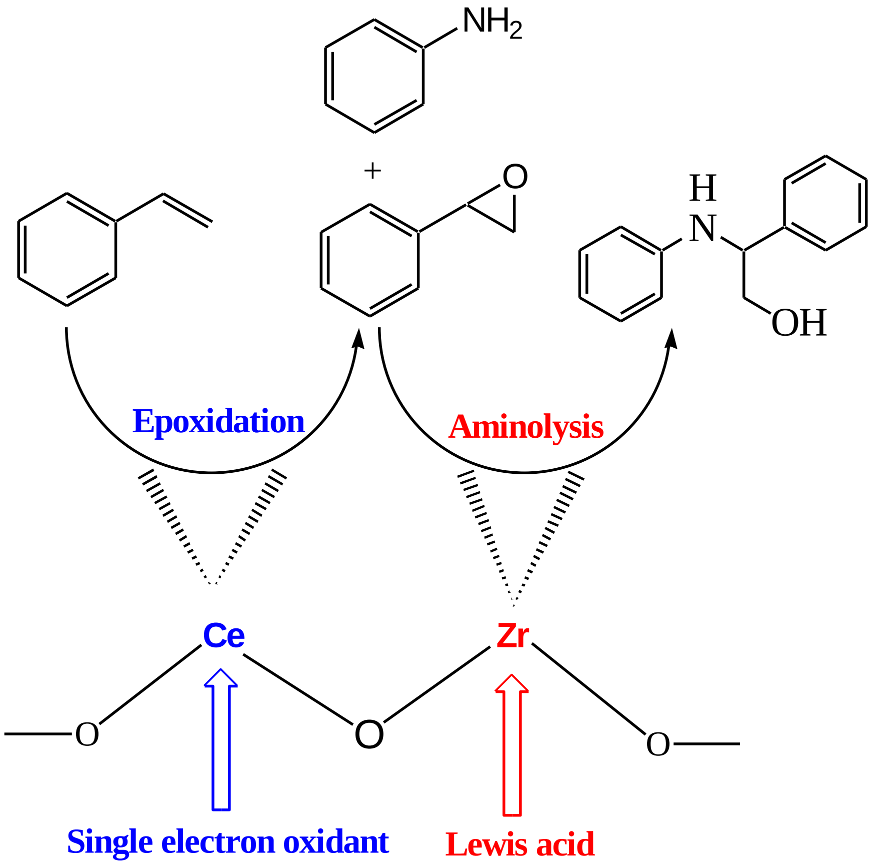
- TiO_2 supported on SO_4^{2-}-ZrO_2
- Pd supported on Heteropolyacids
- Pd supported on MgAl-Hydrotalcites

TiO_2 - SO_4^{2-}/ZrO_2

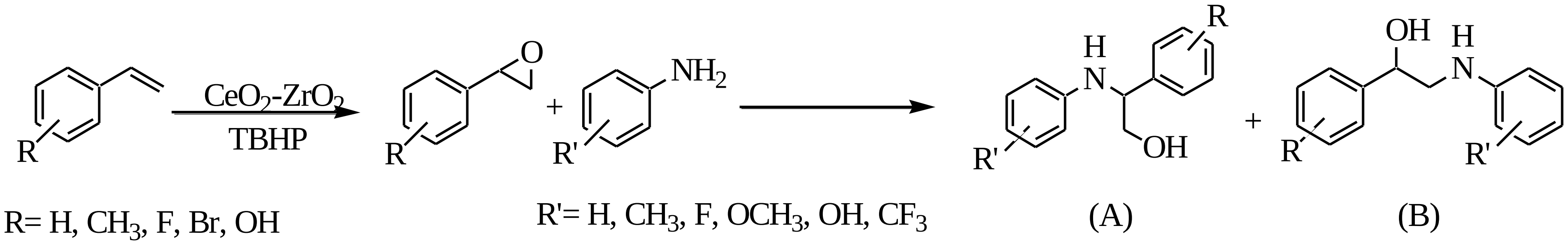


Nur et. al, Journal of Molecular Catalysis A: Chemical 241 (2005) 118–125

CeO_2-ZrO_2 as a **bifunctional** catalyst

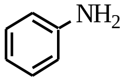
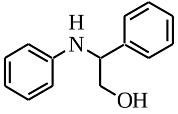
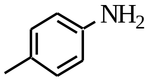
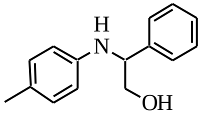
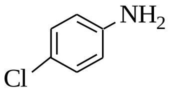
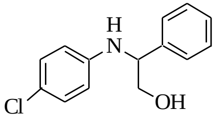
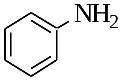
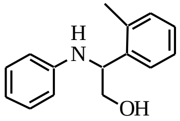
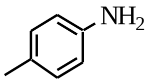
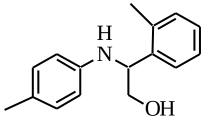
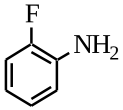
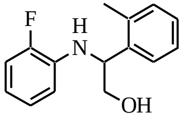


Sequential approach for the synthesis of β-amino alcohols



K. D. Parghi, S. R. Kale and R. V. Jayaram, ***Catalysis Science and Technology, 2012, in press***

CeO_2-ZrO_2 catalyzed sequential epoxidation-aminolysis[a]

Entry	Amine	Amino alcohol	Conversion[b] (%) (A : B)
1[c]			60 (89:11)
2 [c]			61 (90:10)
3 [c]			58 (92:8)
4 [d]			57 (88:12)
5 [d]			60 (91: 9)
6 [d]			59 (92:8)

[a] Reaction conditions- styrene- 2 mmol, TBHP- 4 mmol, 4 mL CCl_4, 20 wt% CeO_2-ZrO_2, 7 h at 80 °C; aniline – 2 mmol added after 7 h and continued for more 7.5 h [b] GC yield [c] alkene = styrene, [d] alkene = 2-methyl styrene

Conclusions

❖Solid acids and bases are green alternatives to conventional catalysts

They have tunable acidity/ basicity and hence can exhibit tremendous selectivity

❖They are robust catalysts and can effect reactions in varied solvents

❖They can be part of bifunctional system thereby reducing process steps

❖In short, soild acids and bases are mile stones in green and clean catalysis

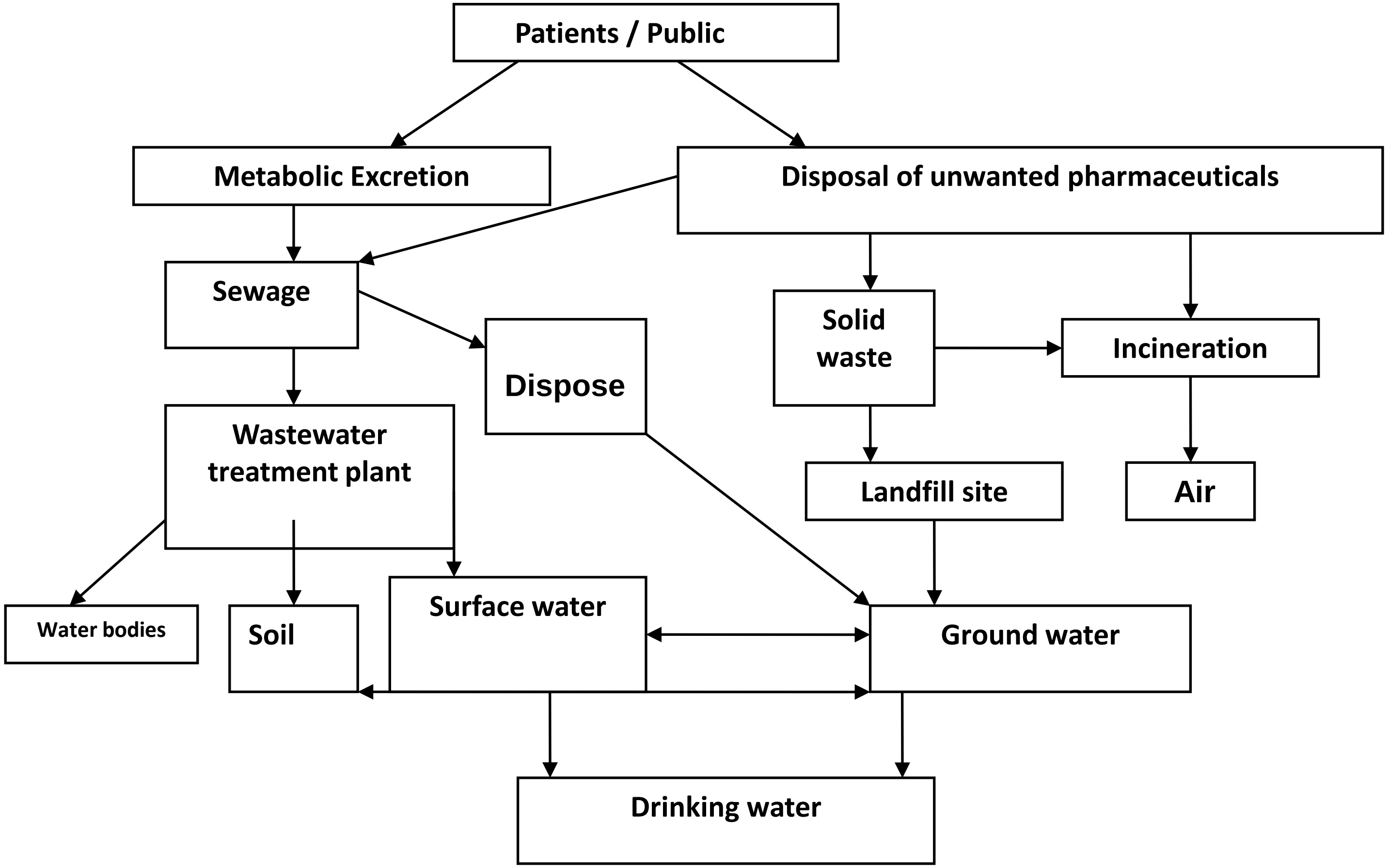
Photocatalysis and Wastewater Treatment

Pharmaceuticals : An Environmental Burden!

- Although the amount of these pharmaceuticals in the aquatic environment is low, their continuous input may constitute in the long- term a potential risk for aquatic and terrestrial organisms.

- Many drugs enter the water bodies through various routes and are present in the ecosystem at levels well above their regulatory levels.

Possible routes of exposure to environment from medications (Gualtero, 2005)



Environmental and health impacts of pharmaceutical drugs

Major concerns

1. Promotion of pathogen resistance to antibiotics.
2. Disruption of endocrine systems.
3. Soil toxicity.
4. Chronic toxic effects leading to irreversible changes in genome.Our focus is on two most commonly used drugs - DICLOFENAC and PARACETAMOL

General Mechanism of Photocatalysis

1. Generation of electron and hole pair

$$\mathbf{SC \rightarrow h^{+} + e^{-}}$$

2. Generation of hydroxyl radicals

$$\mathbf{h^{+} + H_2O \rightarrow {}^{\cdot}OH + H^{+}}$$

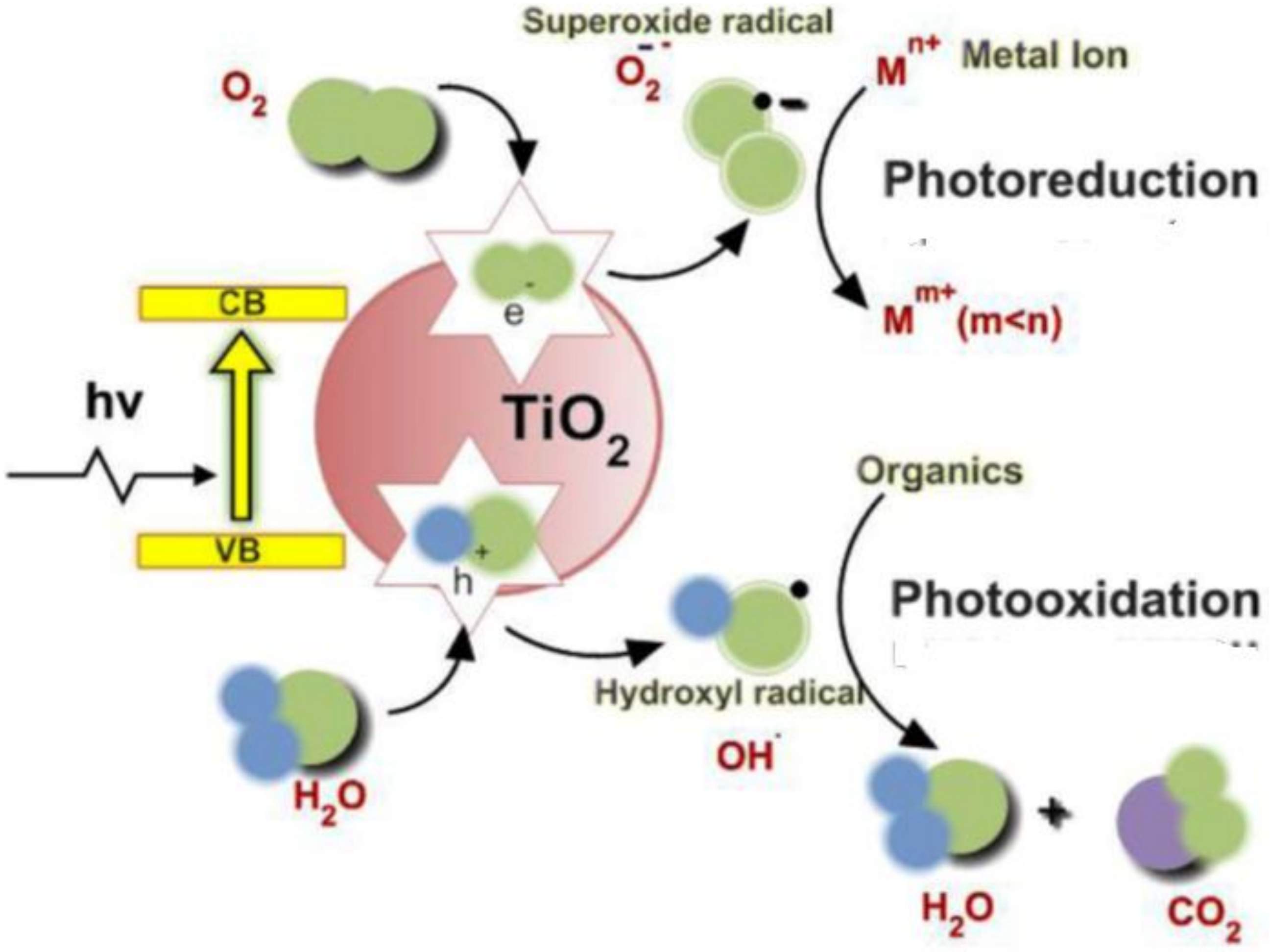
3. Reduction of dissolved oxygen by the photo generated electrons

$$\mathbf{e^{-} + O_2 \rightarrow O_2^{-\cdot}}$$

4. Oxidation of pollutant

$$\mathbf{{}^{\cdot}OH + pollutant \rightarrow Intermediate\ compounds \rightarrow CO_2 + H_2O}$$

TYPICAL PHOTOCATALYTIC PROCESS



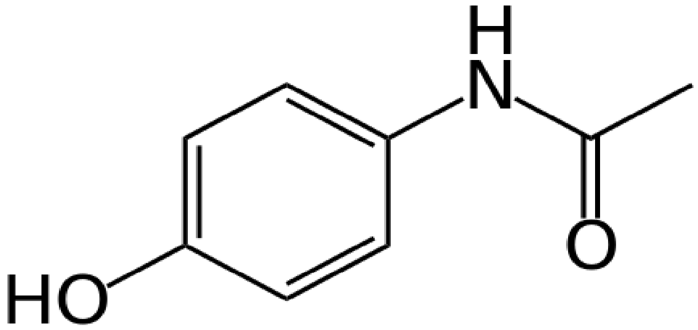
Green Advantages

- The process uses renewable energy.

- The reaction conditions for photocatalysis are mild, the reaction time is modest, and less chemical input is required.

- Catalyst is non-hazardous

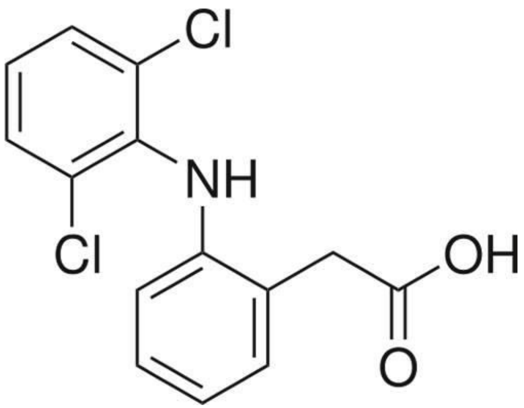
PARACETAMOL



Toxic Effects

- Approximately 58–68% of paracetamol is excreted from the body during therapeutic use.
- When used in excess, it may cause liver failure

DICLOFENAC



Toxic Effects

- Toxicity to liver, kidney
- Highly toxic to vultures leading to its complete ban in India and Pakistan for veterinary use.
- Toxic to many other animal species.

Paracetamol

Catalyst	Rate Constant, k (min^{-1})
Commercial TiO_2	1.31×10^{-2}
ZnO	1.98×10^{-2}
Ag – TiO_2 (1%)	3.01×10^{-2}
Ag – TiO_2 (2%)	4.10×10^{-2}

.Dwoolkar, K. D. and Jayaram, R. V. “Pheotocatalytic degradation of Paracetamol”, International Journal of Biotechnology, Chemical and Environmental Engineering, 2(1), **2013**, 27-32

Diclofenac

Catalyst	Rate Constant, k (min^{-1})
Commercial TiO_2	1.01×10^{-2}
ZnO	1.15×10^{-2}
Ag – TiO_2 (1%)	1.66×10^{-2}
Ag – TiO_2 (2%)	2.15×10^{-2}

Dewoolkar, K. D. and Jayaram, R. V. “Photocatalytic degradation of Diclofenac”, International Journal of Research in Chemistry and Environment, 3(3), **2013,** 94-99.

It always seems impossible until it is done