Part 1. The Earth’s Atmosphere

Additional Chapter 1.

The Air Pollution Solutions

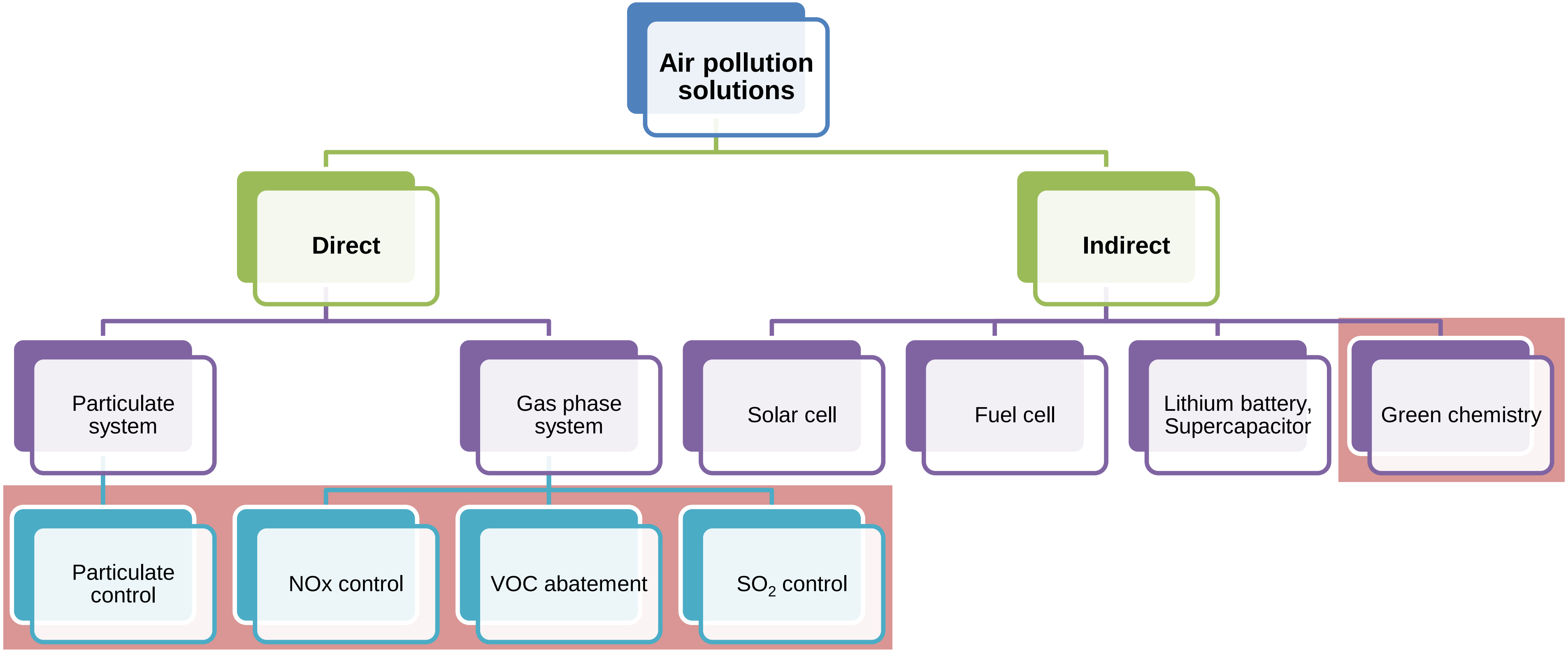
Additional Chapter 1. The Air Pollution Solutions

1.1 Summary of the major air pollutants

Major Air Pollutants			
Pollutant	**Description**	**Sources**	**Effects**
Carbon monoxide (CO)	CO is an odorless, colorless and poisonous gas produced by the incomplete burning of fossil fuels(gasoline, oil, nature gas)	Cars, trucks, buses, small engines, and some industrial processes are major sources. Wood stoves, cigarette smoke, and forest fires are also sources of CO.	CO interferes with the blood`s ability to carry oxygen, slowing reflexes and causing drowsiness. In high concentrations, CO can cause death. Headaches and stress on the heart can result from exposure to CO.
Nitrogen Oxides (NOx)	Nitrogen and oxygen combine during combustion(burning) to form nitrogen oxides. Many nitrogen oxides are colorless and odorless gases	NOx come from burning fuels in motor vehicles, power plants, industrial, commercial, and residential sources that burn fuels	NOx can make the body vulnerable to respiratory infections, lung disease, and possibly cancer. NOx contributes to the brownish haze seen over congested areas and to acid rain. NOx easily dissolves in water and forms acids which can cause metal corrosion and fading/deterioration of fabrics
Sulfur Dioxide (SO_2)	SO_2 is a gas produced by chemical interactions between sulfur and oxygen.	SO2 comes largely from burning fossil fuels(gasoline, oil, natural gas). It is released from petroleum refineries, paper mills, chemical and coal burning power plants	SO2 easily dissolves in water and forms and acid which contributes to acid rain. Lakes, forests, metals, and stone can be damaged by acid rain.
Volatile Organic Compounds (VOCs)	VOCs are organic (contain carbon) compounds that vaporize easily. Gasoline, benzene, toluene, and xylene are examples of VOCs	VOCs are emitted as gases(fumes). Sources of VOCs include burning fuels, solvents, cleaning supplies, paints, and glues. Cars are a major source of VOCs	VOCs contribute to smog formation and can cause serious health problems such as cancer. They may also harm plants.
Particulate matter or Particle pollution	Particulate matter is a term used to describe very small solids. Smoke, ash, soot, dust, lead, and other particles from burning fuels are examples of some of the compounds that make up particulate matter.	Some particles are directly emitted from cars, trucks, buses, factories, construction sites, tilled fields, unpaved roads, and burning wood. Other particles are indirectly formed when gases from burning fuels react with sunlight and water vapor	Particulate matter can reduce visibility and cause a variety of respiratory problems. Particulate matter has also been linked to cancer. It can also corrode metal; erode building and sculptures, and soil fabrics.
Ozone(O_3)	Ozone is a gas not usually emitted directly into the air. Ground level ozone is created by a chemical reaction between NOx and VOCs in the presence of heat and sunlight	Motor vehicle exhaust, industrial emissions, gasoline vapors, and chemical solvents are some of the major sources of NOx and VOCs	Ozone can irritate lung airways and cause wheezing and coughing. Repeated exposure can cause permanent lung damage. Ozone damages leaves of trees and other plants. It decreases the ability of plants to produce and store food, and reduces crop yield

Additional Chapter 1. The Air Pollution Solutions

1.2 The air pollution solutions



Air pollution solutions

Direct

Indirect

Particulate system

Gas phase system

Solar cell

Fuel cell

Lithium battery, Supercapacitor

Green chemistry

Particulate control

NOx control

VOC abatement

SO_2 control

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions

Particulate control
- Mechanical collector (Dust cyclone)
- Electronic precipitators

NOx control
- Low NOx burner
- Selective catalytic reaction (SCR)
- Selective non-catalytic reaction (NSCR)

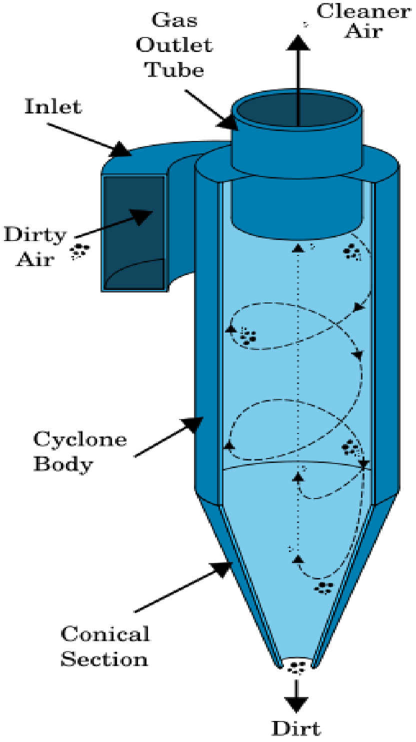
VOC(volatile organic compound) abatement
- Adsorption system

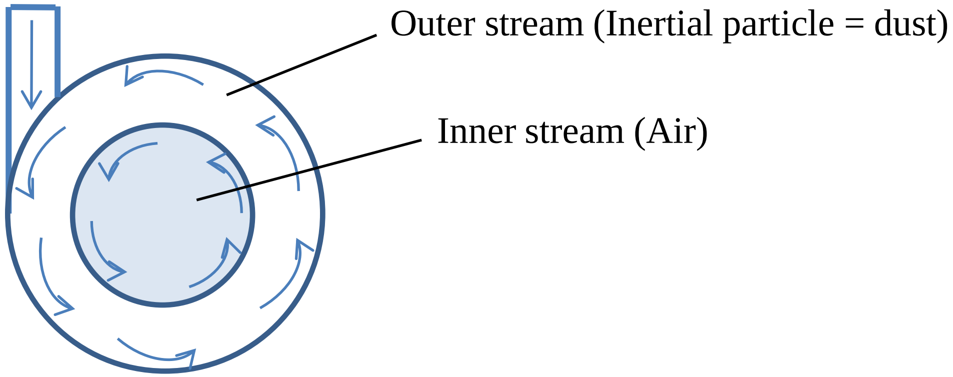
Acid gas/SO_2 control
- Flue gas desulfurization

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : Particulate control (Mechanical collector)

- Dust cyclone





Scheme of standard dust cyclone

- Air flows in a spiral pattern, beginning at the top (wide end) of the cyclone and ending at the bottom (narrow) end before exiting the cyclone in a straight stream through the center of the cyclone and out the top.
- Larger (denser) particles in the rotating air stream have too much inertia to follow the tight curve of the air stream and strike the outside wall, falling then to the bottom of the cyclone where they can be removed. In a conical system, as the rotating air-flow moves towards the narrow end of the cyclone the rotational radius of the air stream is reduced, separating smaller and smaller particles from the air stream.
- The cyclone geometry, together with air flow rate, defines the *cut point* of the cyclone. This is the size of particle that will be removed from the air stream with a 50% efficiency. Particles larger than the cut point will be removed with a greater efficiency, and smaller particles with a lower efficiency.

http://www.fmdaircontrol.com/products.htm

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : Particulate control

- Electrostatic precipitator

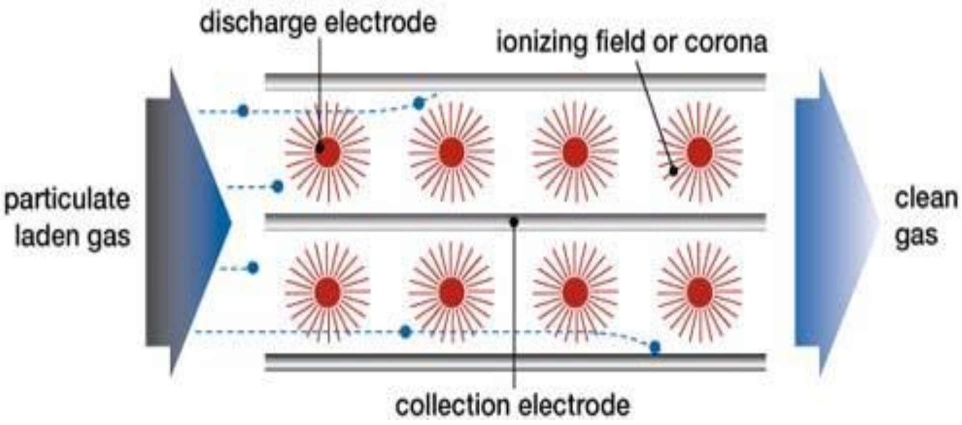


Figure. Top view of ESP schematic diagram

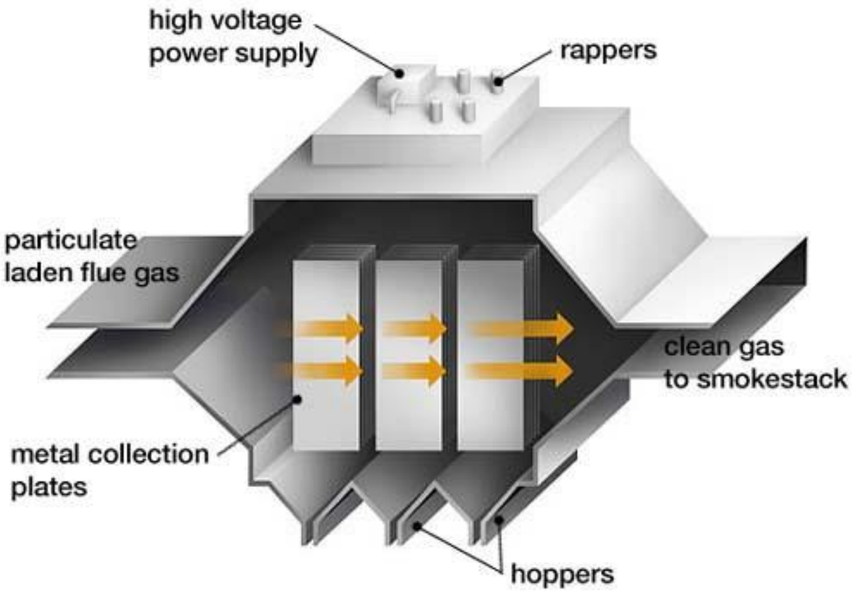


Figure. side view of ESP schematic diagram

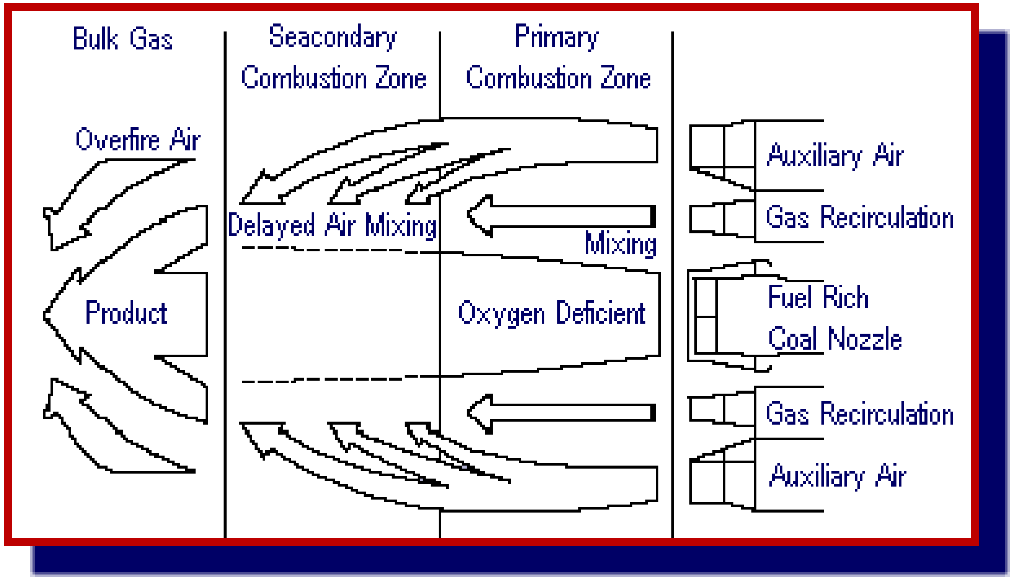
- The most basic precipitator contains a row of thin wires, and followed by a stack of large flat metal plates, with the plates typically spaced about 1 cm apart. The air stream flows through the spaces between the wires, and then passes through the stack of plates.
- A negative voltage of several thousand volts is applied between wire and plate. If the applied voltage is high enough an electric discharge ionizes the air around the electrodes. Negative ions flow to the plates and charge the gas-flow particles.
- The ionized particles, following the negative electric field created by the power supply, move to the grounded plates.
- Particles build up on the collection plates and form a layer. The layer does not collapse, thanks to electrostatic pressure (given from layer resistivity, electric field, and current flowing in the collected layer).
- Electrostatic precipitators have collection efficiency of 99%, but do not work well for flyash with a high electrical resistivity (low-sulfur coal)

http://www.eas.asu.edu/~holbert/wise/electrostaticprecip.html

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : NOx control

- Low NOx burner

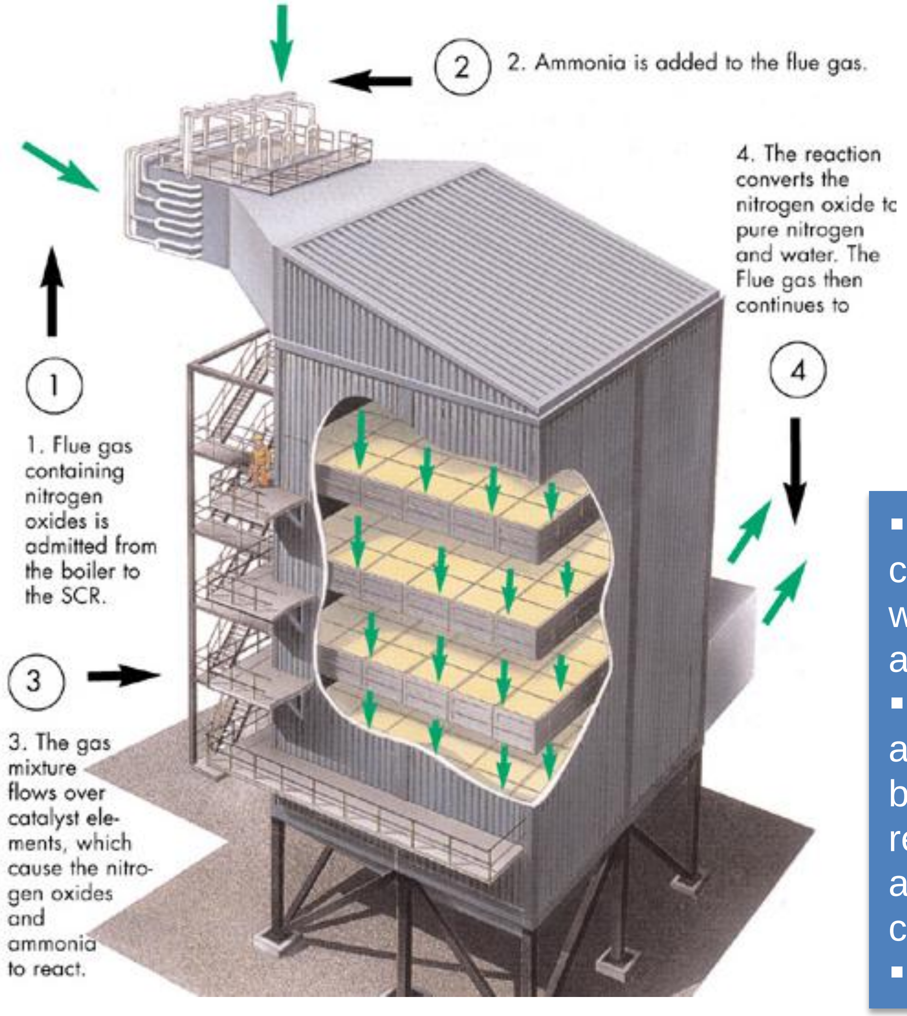


- Low-NOx burners (LNBs) are designed to "stage" combustion. In this technology, a fuel-rich combustion zone is created by forcing additional air to the outside of the firing zone (auxiliary air) and by delaying the combustion of coal. Reduction of 30 to 55 % of NOx can be achieved with low-NOx burners. Advanced stage combustion technologies use overfire air and gas or coal reburning to achieve even greater reductions of NOx .
- The introduction of auxiliary air outside the coal nozzle (right side of figure), which creates an oxygen-deficient region and delayed combustion in the primary and secondary combustion zones (center). Overfire air (left) completes the combustion.
- Overfire air systems introduce 10 to 25 % of the combustion air above the main combustion zone, creating a fuel-rich combustion. Low NOx burner plus OFA can reduce NOx by 40 to 60 percent, and gas or coal reburning can reduce NOx by up to 60 to 70 percent

http://www.worldbank.org/html/fpd/em/power/EA/mitigatn/aqnolow.stm

1.3 The direct air pollution solutions : NOx control

- Selective catalytic reduction (SCR)



The NOx reduction reaction

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$2NO + 4NH_3 + 2O_2 \rightarrow 3N_2 + 6H_2O$$
$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$

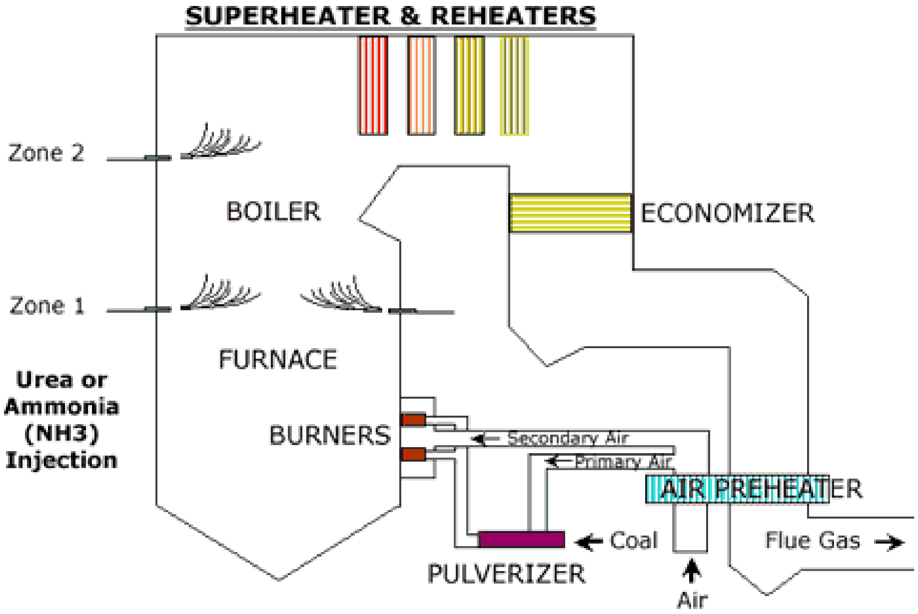
- Selective catalytic reduction (SCR) is a means of converting nitrogen oxides, also referred to as NOx with the aid of a catalyst into diatomic nitrogen, N_2, and water.
- Commercial selective catalytic reduction systems are typically found on large utility boilers, industrial boilers, and municipal should waste boilers. More recent applications include large diesel engines, such as those found on large ships, diesel locomotives, combustion turbines, and even automobiles.
- Removal efficiency : 70 ~ 90%

http://www.dom.com/about/stations/fossil/scr.jsp
대기공학, 동종인 (신광출판사, 서울, 2003)

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : NOx control

- Selective non-catalytic reduction (SNCR)



The NOx reduction reaction

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$2(NH_2)_2CO + 4NO + O_2 \rightarrow 2N_2 + 2CO_2 + 4H_2O$

At too high temperatures ammonia decomposes:

$4NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$

In that case NO is formed instead of reduced.

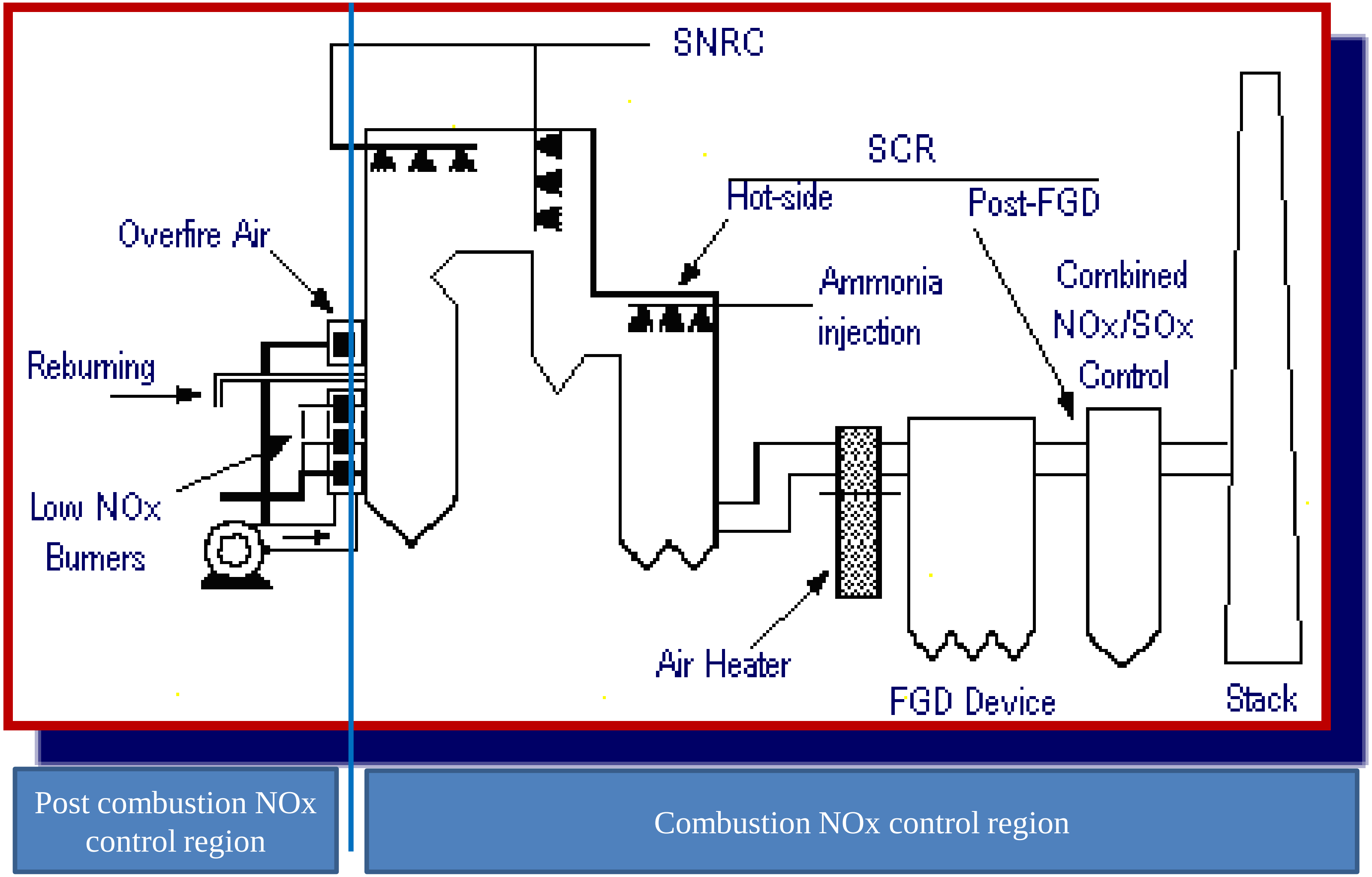
- The process works by injecting a reagent (ammonia or urea) into the radiant and convection regions of a coal fired boiler, furnaces, or other industrial processes where the temperatures favor reactions wherein ammonia reduces NOx to N2.
- The key to the SNCR process is optimization of reagent injection with the flue gas within a specific temperature window. For urea this window is approximately 1800°F-2100°F (982°C-1149°C). For ammonia the window is slightly lower at 1600°F-1800°F (871°C-982°C). The reaction needs a specific temperature window to be efficient. The reaction also needs sufficient reaction time in that temperature window.
- Though in theory selective non-catalytic reduction can achieve the same efficiency of about 90 % as selective catalytic reduction, these practical constraints of temperature, time, and mixing often lead to worse results in practice. However, selective non-catalytic reduction has an economical advantage over selective catalytic reduction, as the cost of the catalyst isn't there.

J. Chem. Engng, 1992, **70**, 1014-1020
http://www.hamon-researchcottrell.com

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : NOx control

- Integrated system for NOx control



Post combustion NOx control region

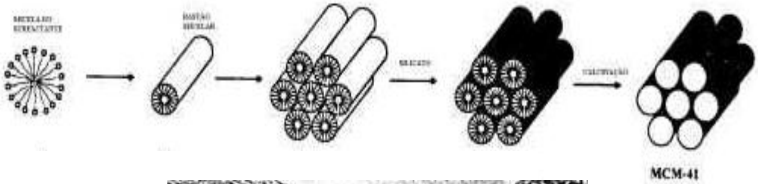
Combustion NOx control region

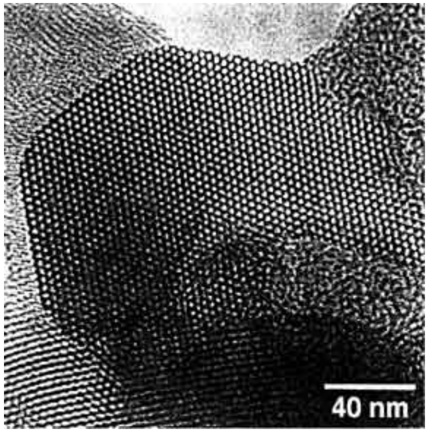
http://www.worldbank.org/html/fpd/em/power/EA/mitigatn/aqnolow.stm

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : VOC abatement (Adsorption system)

- Adsorbents (Zeolite)





MCM-41

- Zeolites are natural or synthetic aluminum silicates which form a regular crystal lattice and release water at high temperature. Zeolites are polar in nature.
- They are manufactured by hydrothermal synthesis of sodium aluminosilicate in an autoclave followed by ion exchange with certain cations (Na+, Li+, Ca++, K+). The channel diameter of zeolite cages usually ranges from 2 to 9 Å (200 to 900 pm).

Table. Properties of the commercial molecular sieve zeolite

Material (Zeolite)	MCM-41	MCM-48	ZSM-5 type CBV 8020	ZSM-5 type CBV 8014
BET surface area(m^2/g)	940~1000	1600	430	415
Pore size(nm)	~4	2~3		
Pore volume(cm^3/g)	0.79	1.2	0.26	0.30
Manufacturer	Mobil Research and Development Corporation, USA	Mobil Research and Development Corporation, USA	Zeolyst, USA	Zeolyst, USA

Nature 2002, **417**, 813-821

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : VOC abatement (Adsorption system)

- Adsorbents (Activated carbon)

- Activated carbon, also called activated charcoal or activated coal, is a general term that includes carbon material mostly derived from charcoal.
- By any name, it is a material with an exceptionally high surface area. Due to a high degree of microporosity, just one gram of activated carbon has a surface area of approximately 500 m², as determined typically by nitrogen gas adsorption.

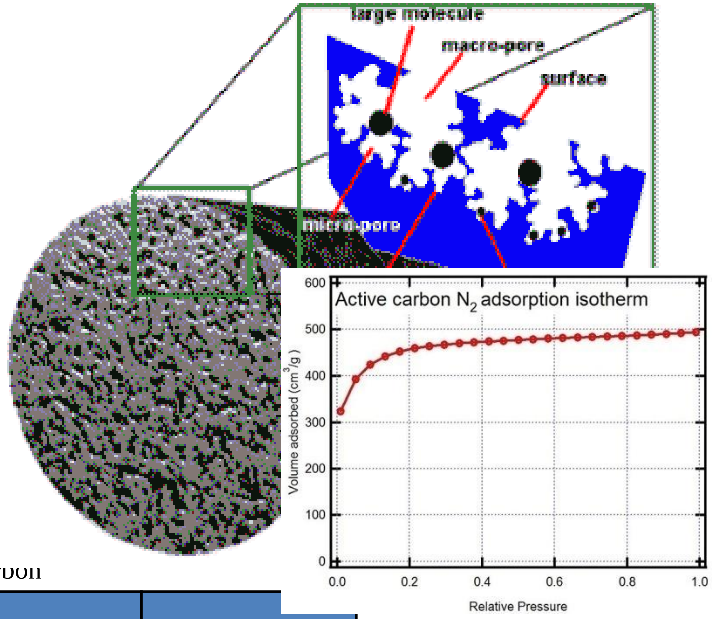


Table. Properties of the commercial activated carbon

Material (Activated carbon)	Darco G-60	Norit A	Darco KB-B
Particle size(mesh)	100-325	200-325	100-325
Surface area(m^2/g)	600	750	1500
Pore volume(cm^3/g)	0.95		2
Moisture(%, max)	12	2	33
Methylene blue adsorption(g/100g, min)	15	12.5	
Ash(%)	3.5	6	
Tamped bulk density(lb/cu ft)	25		28
Fe (ppm, max)	200		100
Phosphates(%, extractable)			0.5
Manufacturer	Sigma-aldrich(USA)	General Norit Co.(Netherland)	Sigma-aldrich(USA)

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : VOC abatement (Adsorption system)

- Ideal candidate for VOC abatement : MCM-41

Table. Characterization Results of the Four Adsorbents

sample	XRD	BET surface area (m^2/g)	total pore volume (mL/g)	BJH pore size distribution (PSD)	pore configuration
Si-MCM-41	$d_{100} = 32.3$ Å	1060	0.87	very narrow PSD centered at 22.5 Å	1-D cylindrical pore, hexagonally packed
hydrophobic zeolite Y	FAU	692	0.31	very narrow PSD centered at 7.4 Å	3-D cage-like pore
silicalite-1 **(ZSM-5)**	MFI	371	0.21	very narrow PSD centered at 5.5 Å	3-D channel-like pore
activated carbon BPL	N/A	923	0.46	bidispersed PSD 8.5 Å, 14.1 Å	Slit-shaped mainly, containing micropores

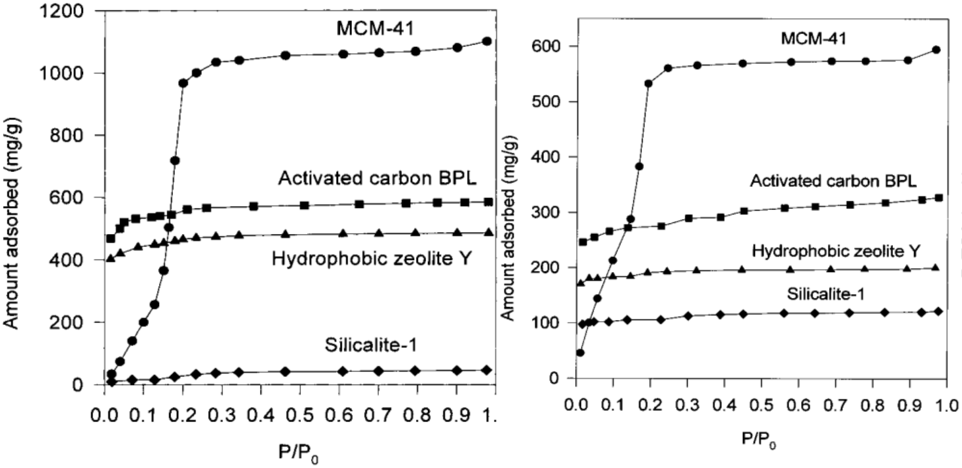


Figure. Adsorption isotherms of carbon tetrachloride(left) and n-hexane(right) over the various adsorbent

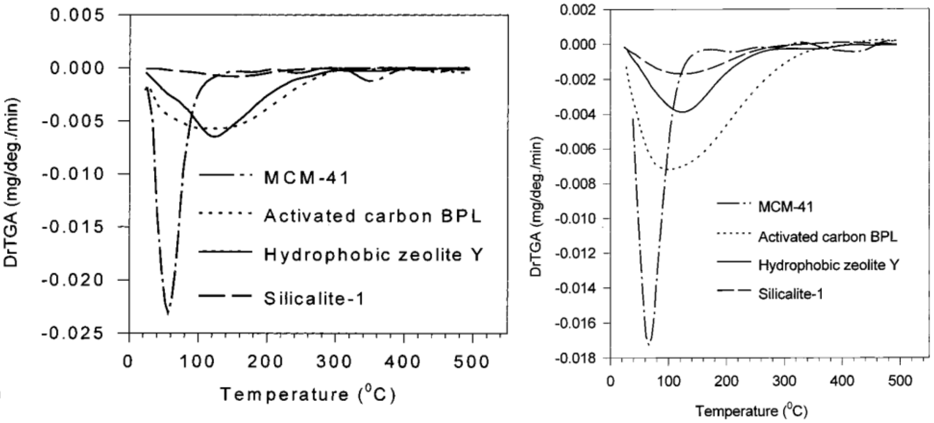


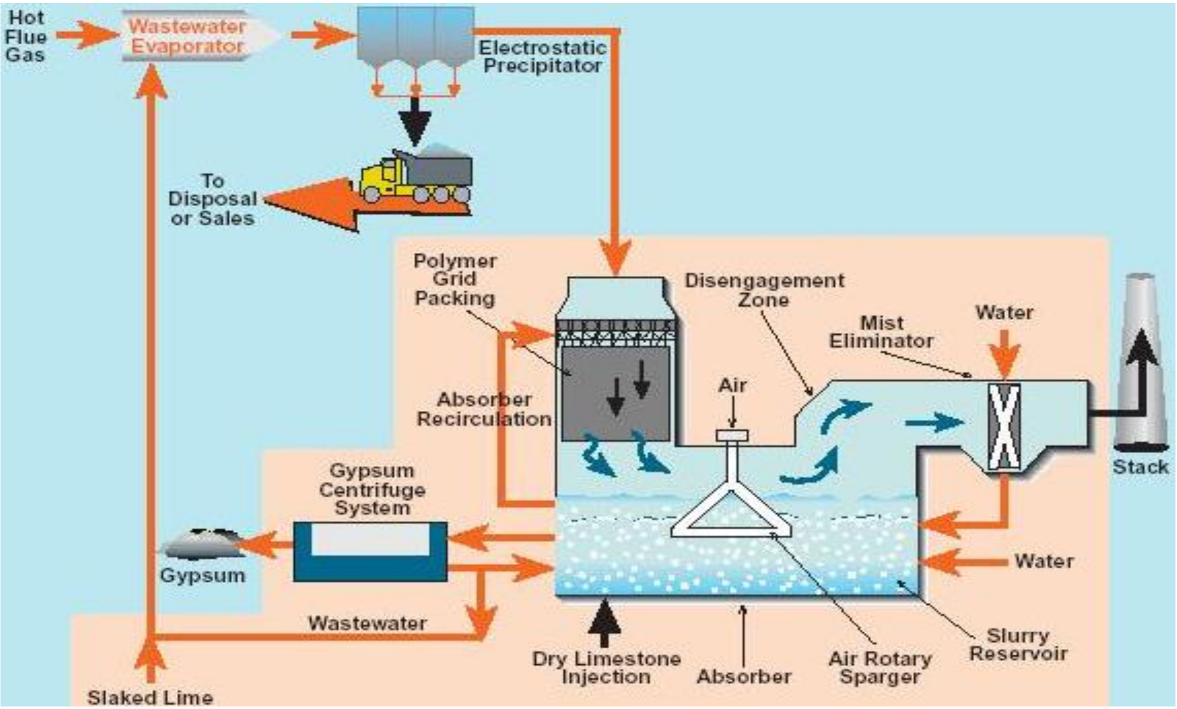
Figure. TPD profiles of carbon tetrachloride(left) and n-hexane(right) from the various adsorbents.

Energy & Fuels 1998, **12**, 1051-1054

Additional Chapter 1. The Air Pollution Solutions

1.3 The direct air pollution solutions : SO_2 control

- Flue gas desulfurization (FGD)



- SO_2 is an acid gas and thus the typical sorbent slurries or other materials used to remove the SO_2 from the flue gases are alkaline.
- The reaction taking place in wet scrubbing using a $CaCO_3$ (limestone) slurry produces $CaSO_3$ (calcium sulfite) and can be expressed as:

  $CaCO_3$ (solid) + SO_2 (gas) -> $CaSO_3$ (solid) + CO_2 (gas)
- When wet scrubbing with a $Ca(OH)_2$ (lime) slurry, the reaction also produces $CaSO_3$ (calcium sulfite) and can be expressed as:

  $Ca(OH)_2$ (solid) + SO_2 (gas) -> $CaSO_3$ (solid) + H_2O (liquid)
- When wet scrubbing with a $Mg(OH)_2$ (magnesium hydroxide) slurry, the reaction produces $MgSO_3$ (magnesium sulfite) and can be expressed as:

  $Mg(OH)_2$ (solid) + SO_2 (gas) -> $MgSO_3$ (solid) + H_2O (liquid)
- Some FGD systems go a step further and oxidize the $CaSO_3$ (calcium sulfite) to produce marketable $CaSO_4 \cdot 2H_2O$ (gypsum)

  $CaSO_3$ (solid) + ½O_2 (gas) + $2H_2O$ (liquid) -> $CaSO_4 \cdot 2H_2O$ (solid)

http://rebar.ecn.purdue.edu/ECT/Fimages

Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (Principles)

Principles

- The use of safe, environment-benign substances, including solvents, whenever possible
- The design of energy efficient processes
- The best form of waste disposal: do not create it in the first place

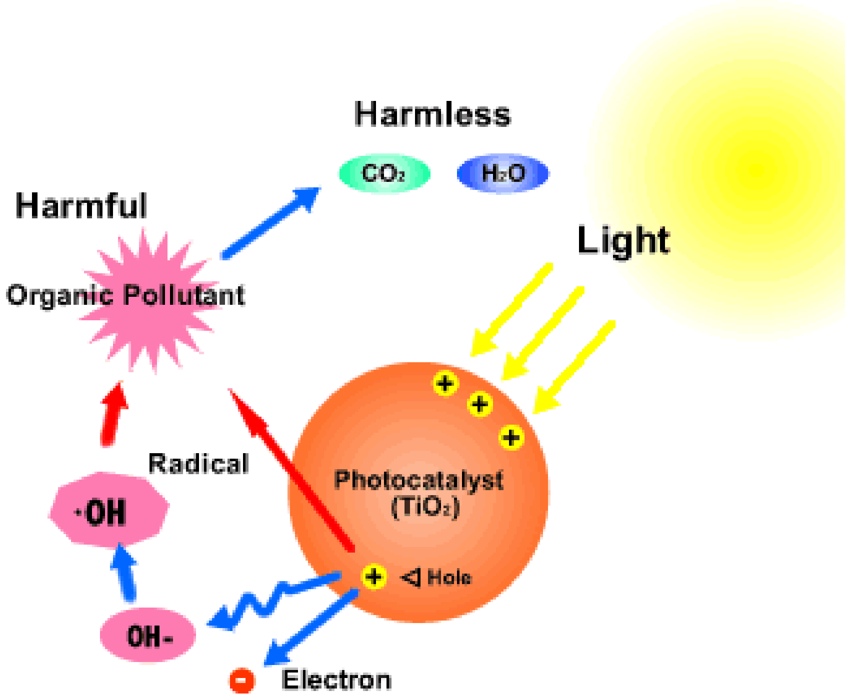
I. Prevent waste
II. Design safer chemicals and products
III. Design less hazardous chemical syntheses
IV. Use renewable feedstock
V. Use catalysts, not stoichiometric reagent
VI. Avoid chemical derivatives.
VII. Maximize atom economy.
VIII. Use safer solvents and reaction conditions
IX. Increase energy efficiency
X. Design chemicals and products to degrade after use
XI. Analyze in real time to prevent pollution
XII. Minimize the potential for accidents.

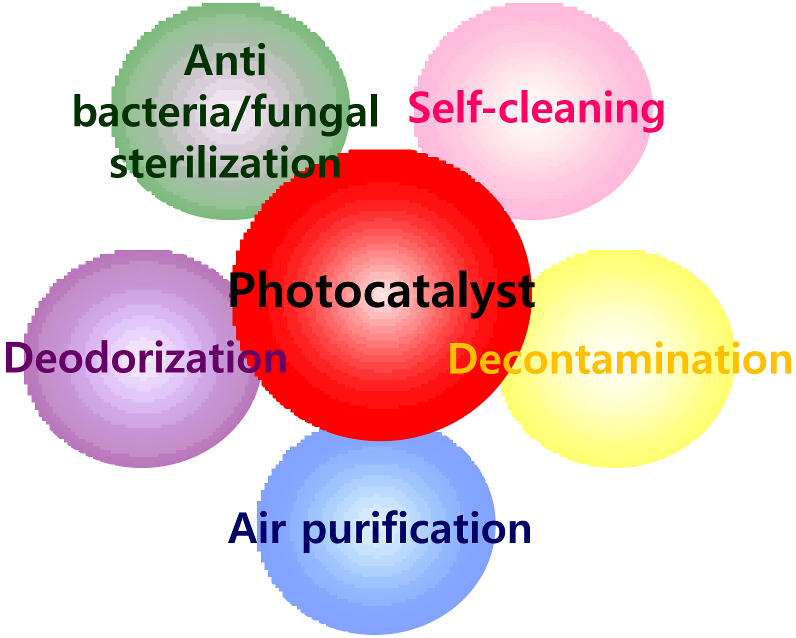
Green chemical syntheses and processes, ed. Paul T. Anastats (ACS, Washington, D.C., 2000).
www.evp.org

Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (photocatalyst)

- TiO_2 based photocatalyst




Anti bacteria/fungal sterilization

Self-cleaning

Photocatalyst

Deodorization

Decontamination

Air purification

- A solid that can promote reactions in the presence of light and is not consumed in the overall reaction
- Photoactive, able to utilize visible and/or UV light, biologically and chemically inert, photostable, inexpensive, non-toxic
- Photocatalytic activity (PCA) is the ability of a material to create an electron/hole pair as a result of exposure to ultraviolet radiation.
- The resulting free-radicals are very efficient oxidizers of organic matter.

Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (photocatalyst)

- TiO_2 based photocatalyst

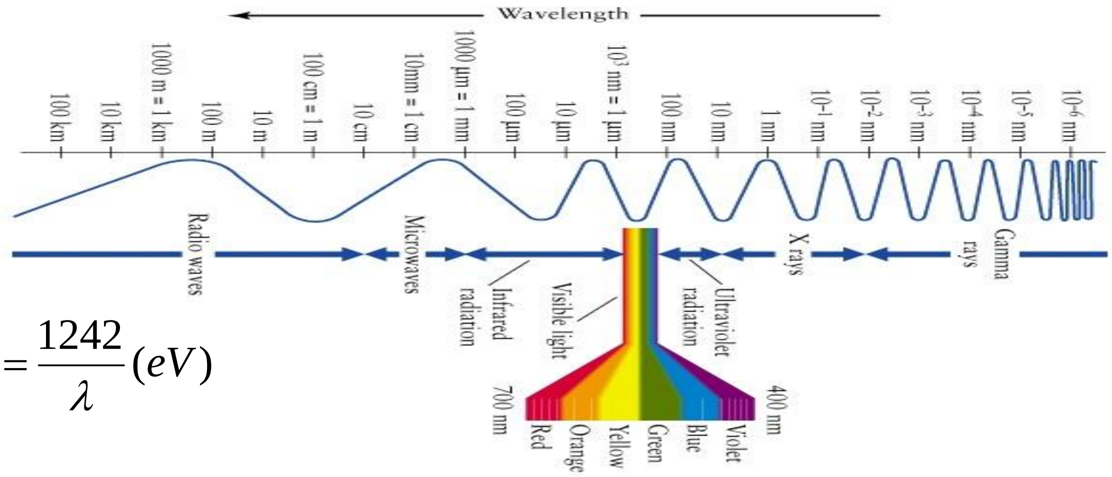
$$\Delta E = E_2 - E_1 = E_g = h\nu = \frac{hc}{\lambda}$$

$$h = 6.626\times10^{-24}\,J\cdot s$$

$$c = 2.998\times10^{8}\,m/s$$

$$E_g = \frac{6.626\times10^{-34}\,J\cdot s\times2.998\times10^{8}\,m/s}{\lambda\times1.6\times10^{-19}\,J/eV} = \frac{1242}{\lambda}(eV)$$

$$\therefore \lambda = \frac{1242}{E_g}(nm)$$



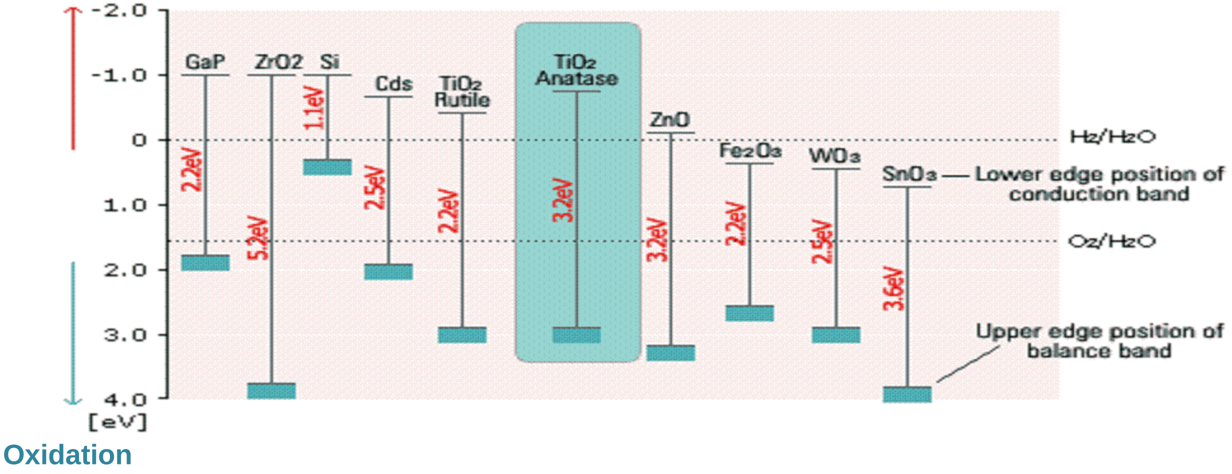
TiO_2 Anatase (E_g=3.2eV)

$$\lambda = \frac{1242}{E_g} = \frac{1242}{3.2} = 388nm$$

TiO_2 Rutile (E_g=3.0eV)

$$\lambda = \frac{1242}{E_g} = \frac{1242}{3.0} = 414nm$$

Band structure of semiconductors

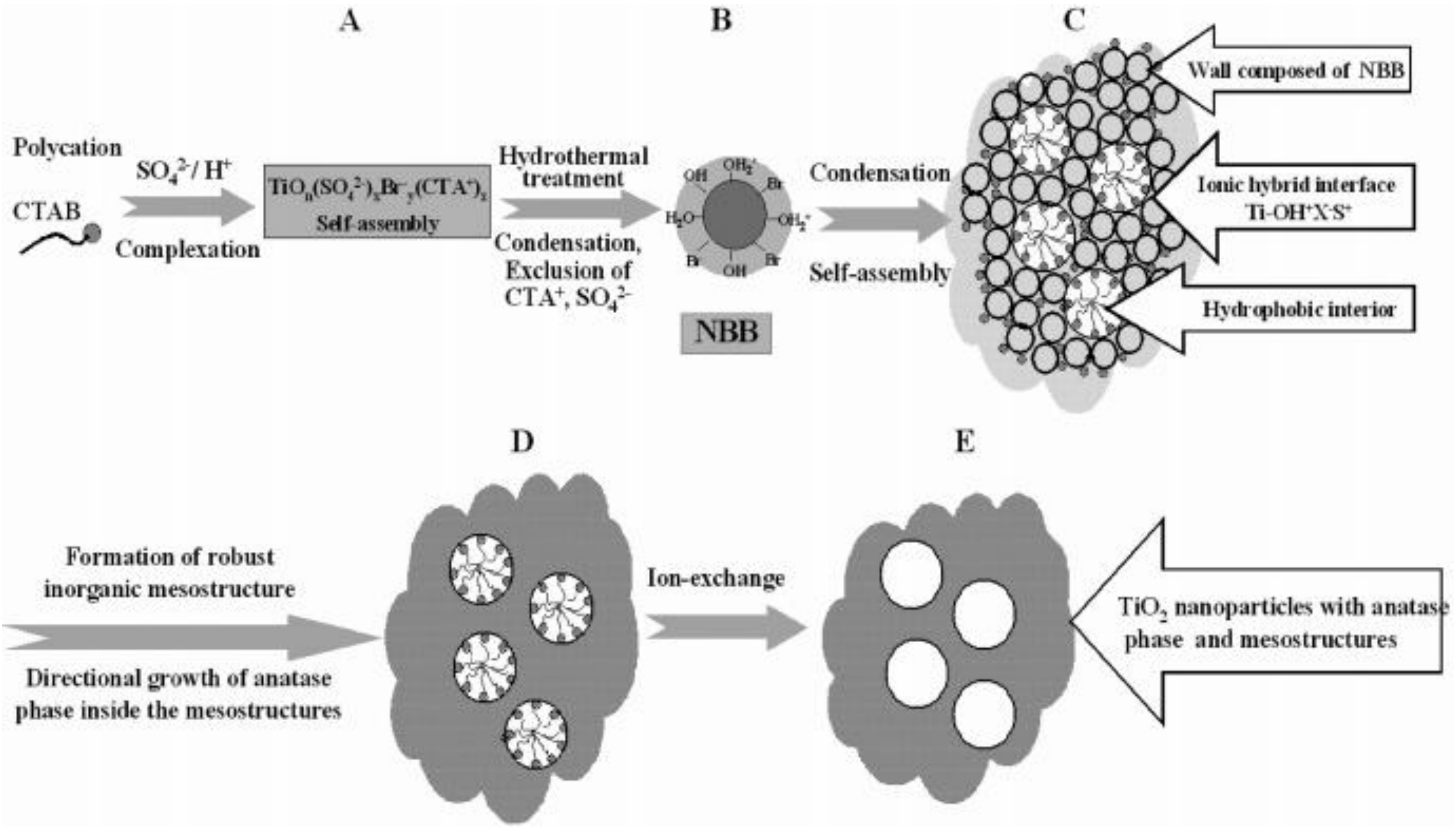


Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (photocatalyst)

- Hot topic : TiO_2 nanoparticles with mesoporous anatase wall

SCHEME : Idealized Formation Model of Mesoporous TiO2 Nanopowders



J. Phys. Chem. B 2005, **109**, 4947-4952

Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (Photocatalyst)

- Hot topic : TiO_2 nanoparticles with mesoporous anatase wall

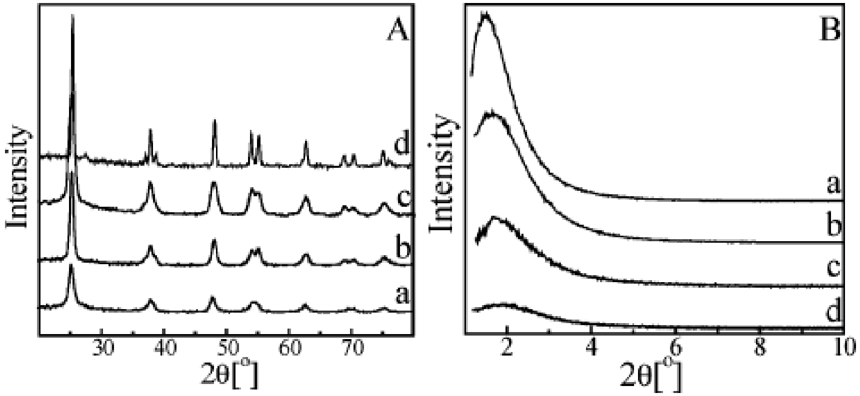


Figure. High-angle (A) and low-angle (B) XRD patterns of samples.
(a) As-synthesized and calcined at (b) 400 °C, (c) 600 °C, (d) 800 °C.

TABLE. Summary of the Physicochemical Properties of Mesoprous TiO2 Nanosized Powders

calcination temp (°C)	crystal size (nm)	S_{BET} (m^2/g)	mean pore size (nm)	total volume (cm^{-3}/g)
as-synthesized	2.3	438.3	2.1	0.56
400	3.1	317.5	2.5	0.61
600	4.2	221.9	2.8	0.50
800	7.5	71.5		0.32

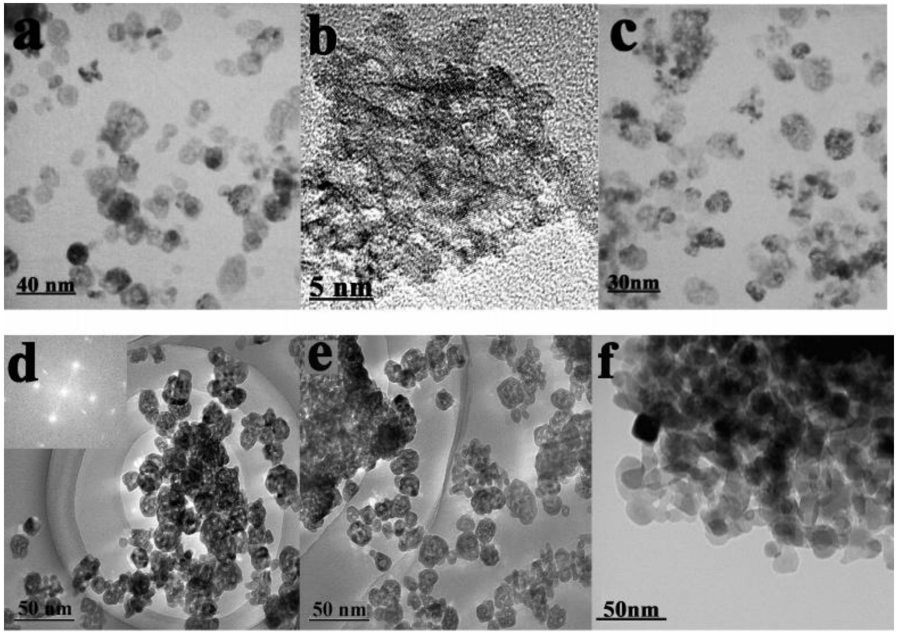


Figure. TEM and HRTEM images of samples. (a), (b) As-synthesized; (c), (d) calcined at 400 °C, (e) 600 °C, and (f) 800 °C.

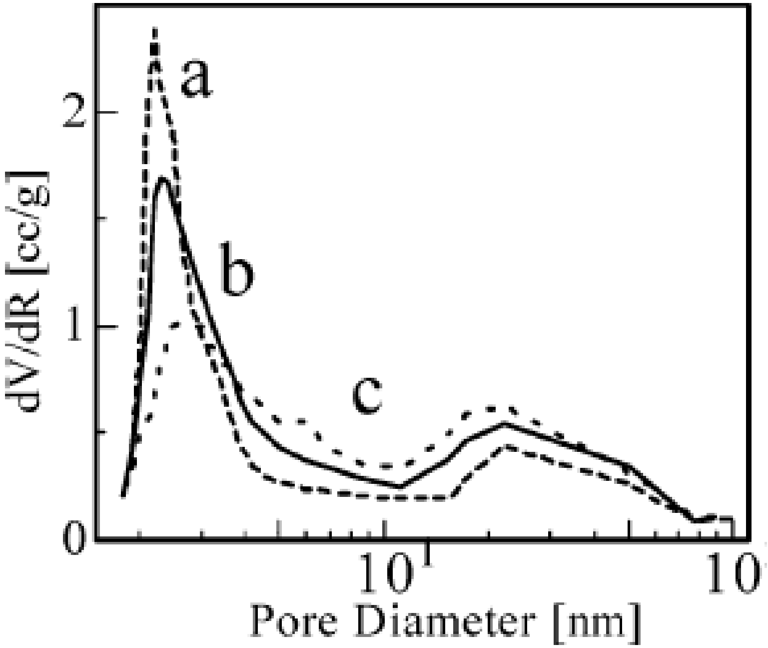


Figure. BJH pore size distribution plots of samples.
(a) As-synthesized and calcined at (b) 400 °C, (c)600 °C.

J. Phys. Chem. B 2005, **109**, 4947-4952

Additional Chapter 1. The Air Pollution Solutions

1.3 The indirect air pollution solutions : Green chemistry (Photocatalyst)

- Hot topic : TiO_2 nanoparticles with mesoporous anatase wall

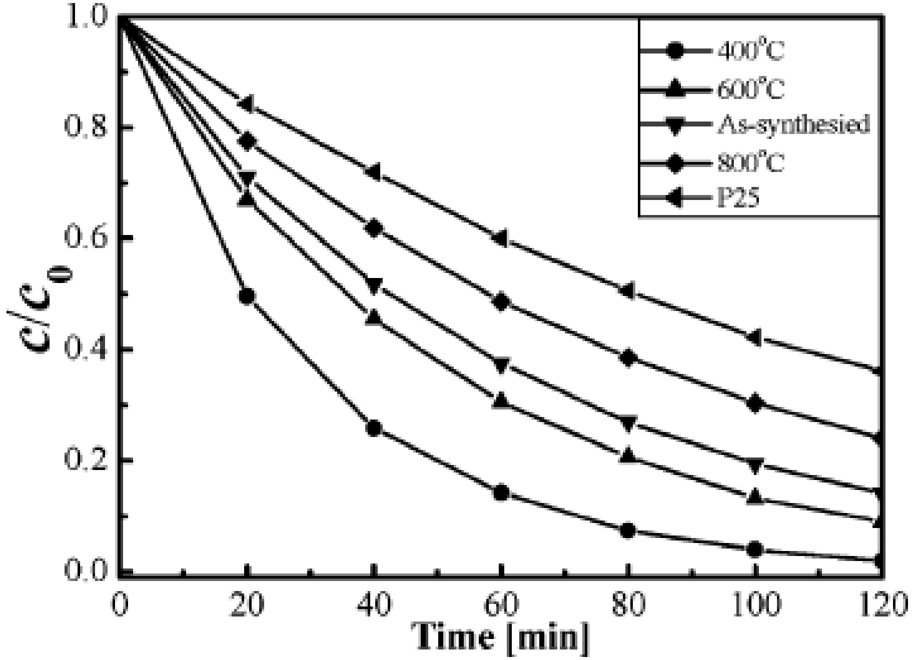


Figure 5. The photocatalytic properties of mesoporous TiO2 samples as prepared and calcined at different temperature as well as the P25 nanoparticles (RB, c0) 1.0 10-5 M, pH 6.0) under UV-light radiation with increasing irradiation time.

- Hydrothermal treatment crystallized powders into anatase without destroying the mesostructure and increased the surface area of the powders significantly
- The mesoporous TiO2 nanopowders exhibit higher photocatalytic activity than the commercial nonporous photocatalyst P25
- The high photocatalytic activity of the calcined mesoporous TiO2 nanosized powders is related to its larger surface area, its smaller anatase crystalline size, and the high crystallinity of the high thermal stable mesostructure TiO2.

J. Phys. Chem. B 2005, **109**, 4947-4952

1.4 The indirect air pollution solutions : Green chemistry (Solvent-free syntheses)

- Microwave-assisted organic synthesis

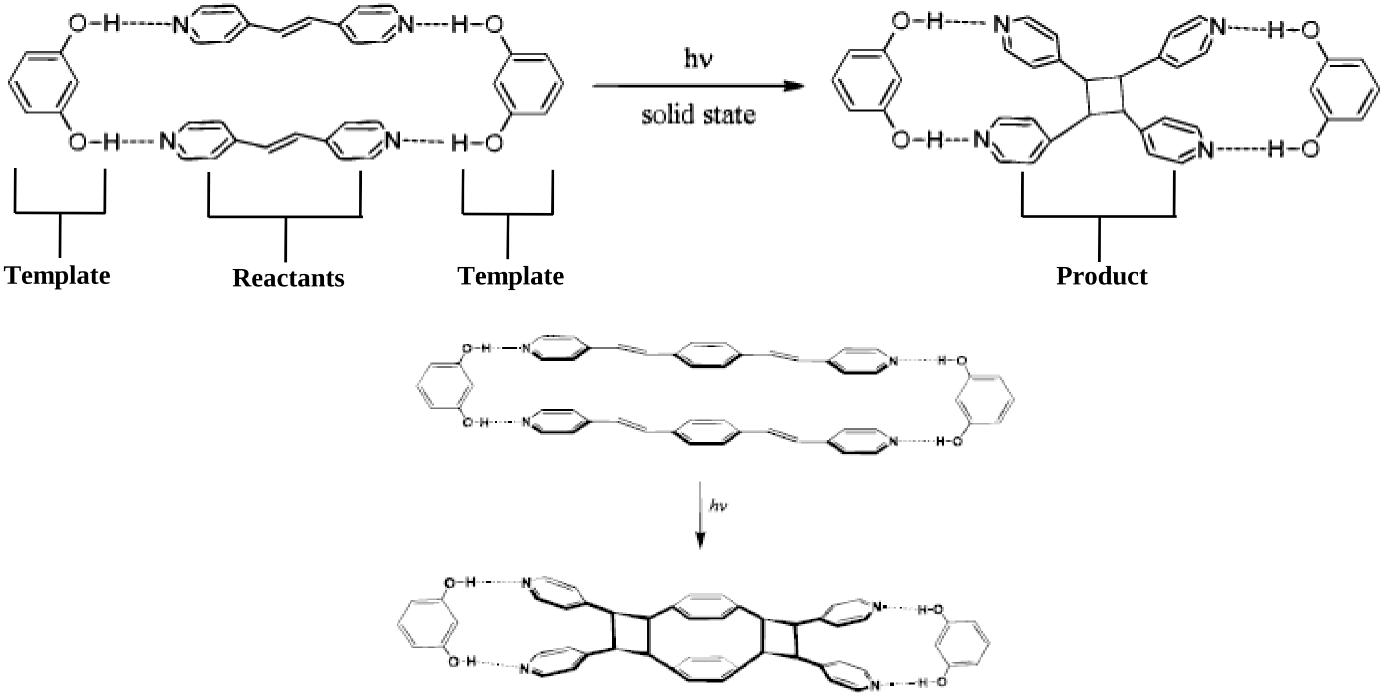


Figure. Supramolecular control of reactivity in the solid state using linear molecular templates

- Microwave-expediated solvent-free synthetic processes involve the exposure of neat reactant to microwave (MW) irradiation in the presence of supported reagents or catalysts on mineral oxides.
- High yield protocols, enhanced reaction rates, greater selectivity and the experimental ease of manipulation are highlighted.
- The recyclability of support materials and their application under solvent-free condition render these processes truly eco-friendly clean protocols

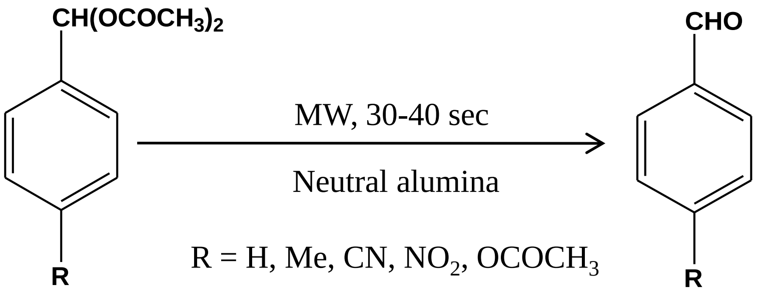
J. Am. Chem. Soc. 2000, **122**, 7817-7818

Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (Solvent-free syntheses)

- Microwave-assisted organic synthesis

Protection/deprotection reactions

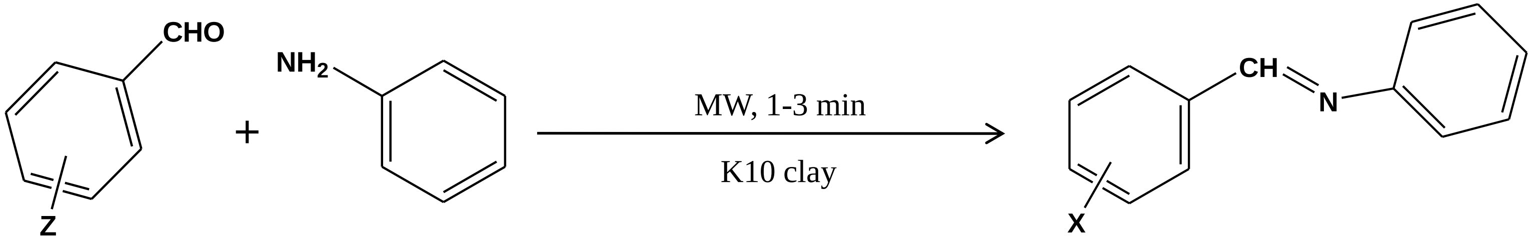


R = H, Me, CN, NO_2, $OCOCH_3$

Figure. Cleavage of aldehyde diacetates

Tetrahedron Lett., 1993, **34**, 3207-3210

Condensation reactions

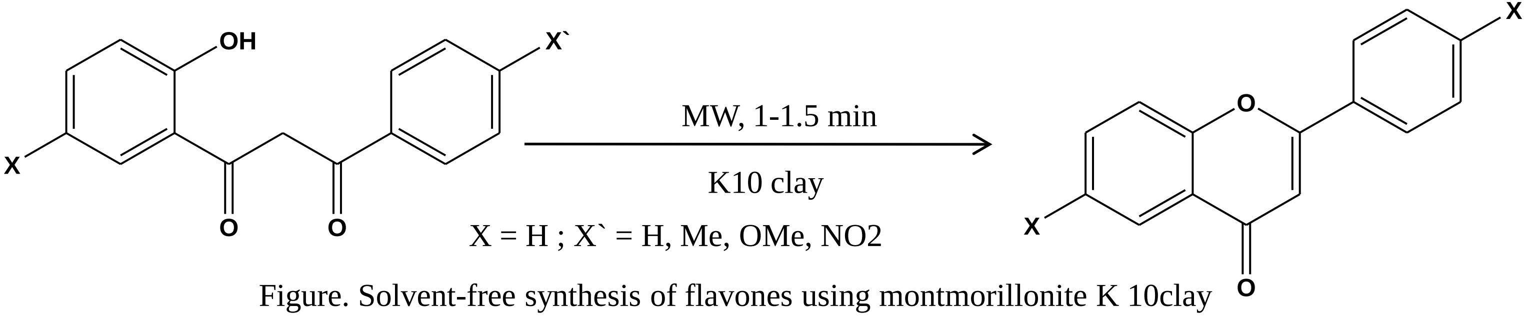


Z = H, *o*-OH, *p*-OH, *p*-Me, *p*-OMe, *p*-NMe_2

Figure. Dehydration reactions using montmorillonite K 10clay

Tetrahedron Lett., 1997, **38**, 2039-2040

Synthesis of heterocyclic compounds



X = H ; X` = H, Me, OMe, NO2

Figure. Solvent-free synthesis of flavones using montmorillonite K 10clay

J. Chem. Res. (S), 1998, 120-121

Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (Metathesis)

- The nobel prize in chemistry 2005 : Green chemistry (metathesis)

Richard R. Schrock

Yves Chauvin

Robert H. Grubbs

Metathesis – a change-your-partners dance

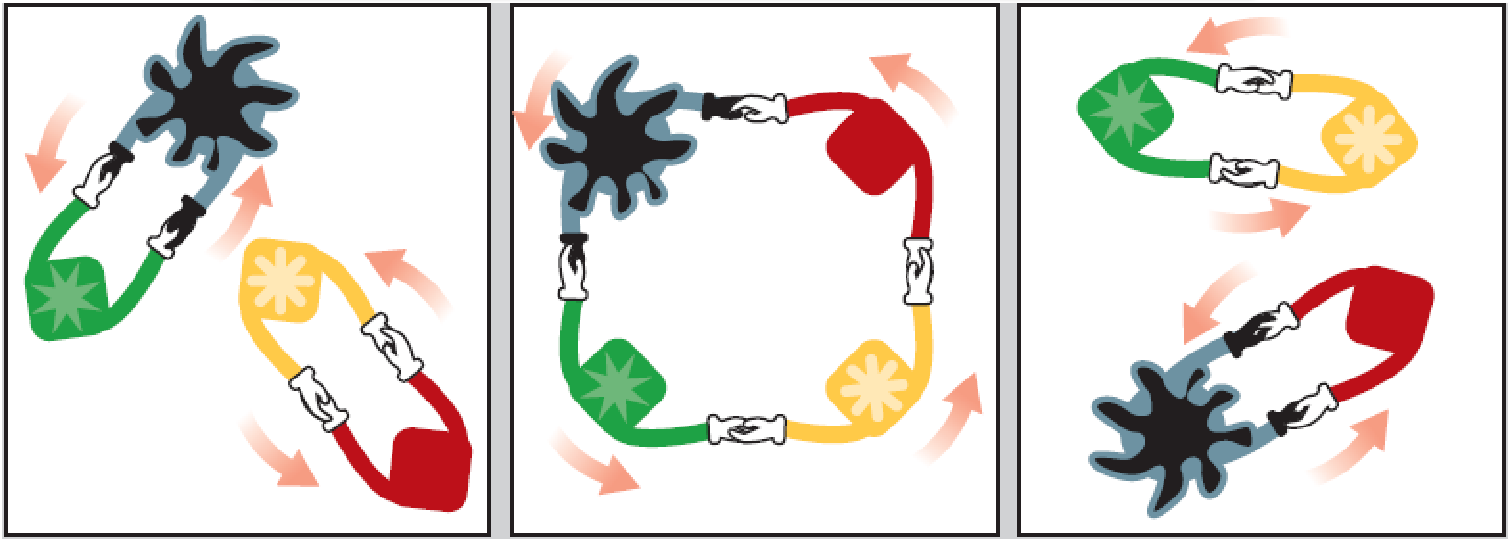


Figure. Chauvins' mechanism described above can be viewed as a dance in which the "catalyst pair" and the "alkene pair" dance round and change partners with one another. The metal and its partner hold hands with both hands and when they meet the "alkene pair" (a dancing pair consisting of two alkylides) the two pairs unite in a ring dance. After a while they let go of each other's hands, leave their old partners and dance on with their new ones. The new "catalyst pair" is now ready to catch another dancing "alkene pair" for a new ring dance or, in other words, to continue acting as a catalyst in metathesis.

www.nobelprize.org

Additional Chapter 1. The Air Pollution Solutions

1.4 The indirect air pollution solutions : Green chemistry (Metathesis)

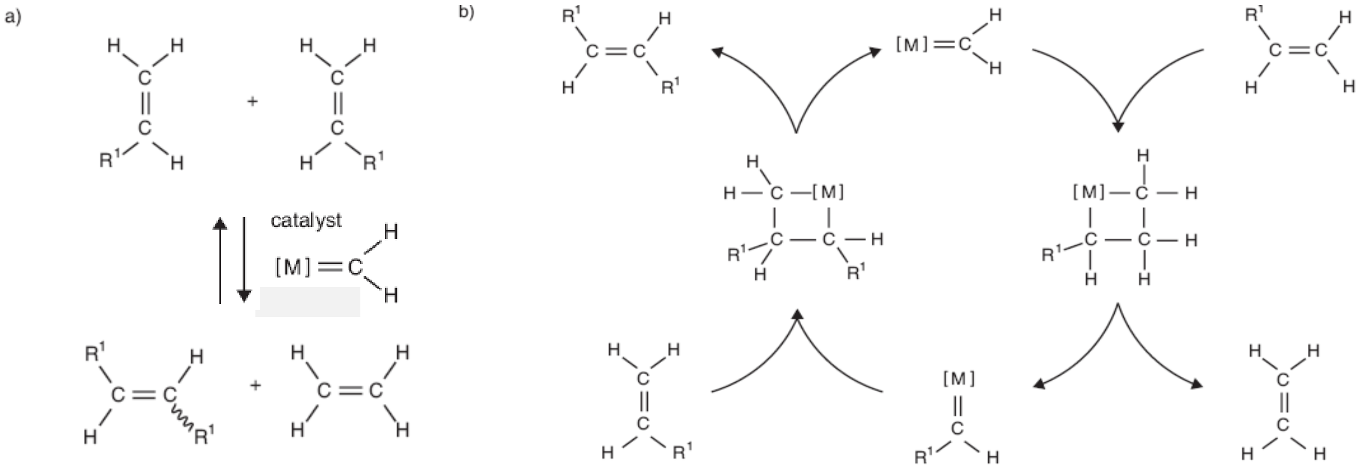


Figure. (a) Metathesis of alkenes catalysed by a metal alkylide. The products are two new alkenes – ethene and the alkene with two R1 groups – one on each carbon in the double bond. The wavy bond shows that the R1 groups can be located on the same side of the double bond or on different sides. (b) Chauvin's mechanism for olefin metathesis. In the catalytic cycle on the way to the products rings with four atoms are formed – three carbons and one metal.

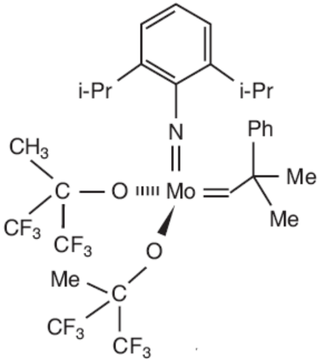


Figure. One of schrock`s molybdenum catalysts. High reactivity has been achieved with the specially-selected groups bound to the metal atom

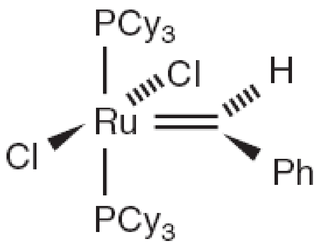


Figure. Ruthenium catalyst developed by Grubbs

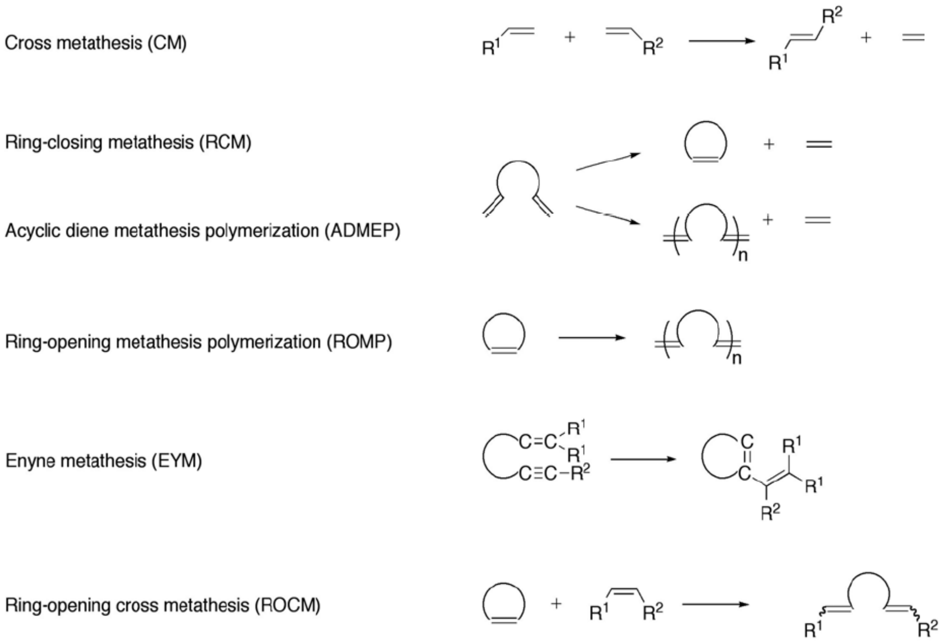
Metathesis is used daily in the chemical industry, mainly in the development of pharmaceuticals and of advanced plastic materials. Thanks to the Laureates' contributions, synthesis methods have been developed that are

- more efficient (fewer reaction steps, fewer resources required, less wastage),
- simpler to use (stable in air, at normal temperatures and pressures) and
- environmentally friendlier (non-injurious solvents, less hazardous waste products).

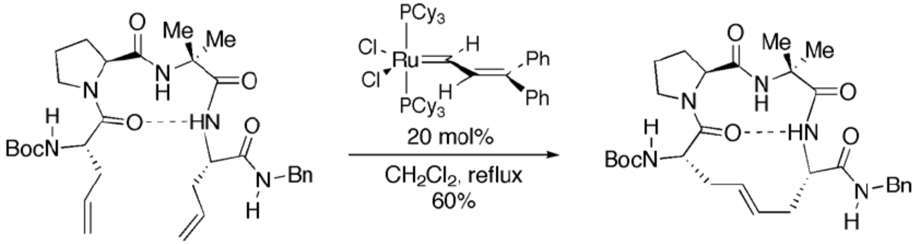
Additional Chapter 1. The Air Pollution Solutions

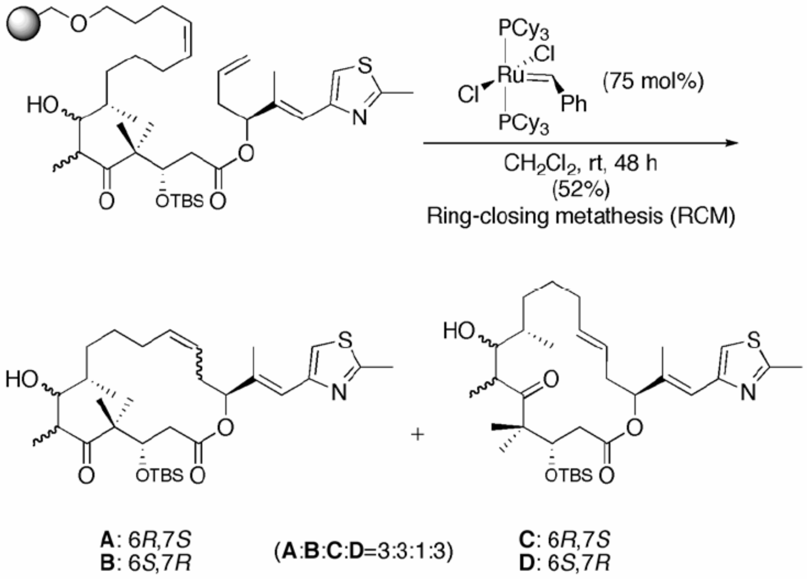
1.4 The indirect air pollution solutions : Green chemistry (Metathesis)

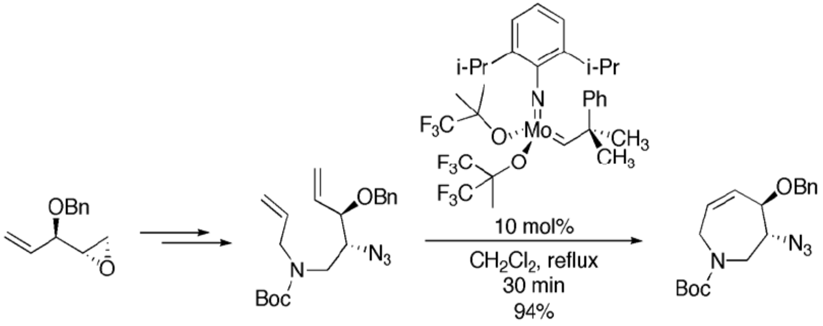
- **The multitude of applications**



Scheme 6







J. Org. Chem., 2000, **65**, 1738
J. Am. Chem. Soc., 1996, **118**, 9606
Nature, 1997, **387**, 268
Chem. Eur. J., 1997, **3**, 441
Angew. Chem. Int. Ed., 2001, **40**, 1452