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Industrial Applications of Zeolites

After having revolutionized the petroleum industry in the fifties, numerous other applications of synthetic zeolites have been found. Today new experimental strategies are helping to start a second revolution : the synthesis of fine chemicals using zeolites.

After a general presentation of what a zeolite is, this article gives a survey of the major industrial applications of this material as molecular sieve, ion exchanger and catalyst. The use of zeolites in the synthesis of intermediates and fine chemicals is emphasized by the presentation of several examples.

A selection of new research directions will be presented at the end. The following topics are considered : new large pore zeolites, microporous solids, the use of computer modelling techniques, the potential of the zeolite's unique electronic properties and the advances toward enzyme type catalysis.

What is a zeolite ?

Zeolites were first recognized by the Swedish mineralogist Crönstedt as a new type of mineral in 1756. Their name was derived from the Greek : zeo, to boil and lithos, the stone.

Zeolites are a class of naturally occurring or synthetic crystalline aluminosilicate minerals. They have 3-D structures arising from a frame work of SiO_4 and AlO_4 tetrahedra (Figure 1), connected through their corners of shared oxygen atoms to form polyhedra (Figure 2), called secondary building units (SBU) [1].

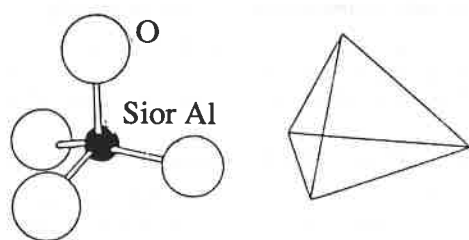


FIGURE 1. - Representations of SiO_4 and AlO_4 tetrahedra.

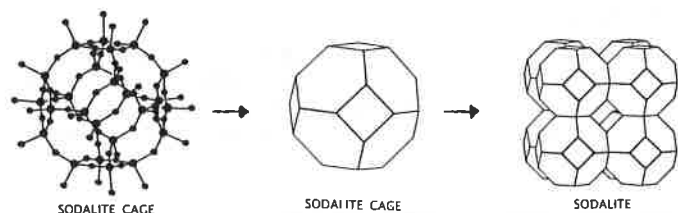


FIGURE 2. - The framework structure of sodalite.

Ball-shaped atoms are omitted, each line represents an oxygen atom and each junction a silicon or aluminum atom. The SBUs are connected to form a very open framework containing channels and cavities in which cations and water

molecules are located. As can be seen in figure 3, different SBUs form different frameworks with specific channel organization.

The cations have a high degree of mobility
 → ion exchange properties

The water molecules are readily lost or regained
 → desiccant properties.

The porous structure induces regular arrays or apertures able to take up selectively some molecules into the pores while rejecting others on the basis of their large effective molecular dimensions
 → unique property of "molecular-sieving".

Essential basic properties of zeolites are summarized in Table I.

TABLE I. - General characteristics of zeolites.

Chemical formula	$\text{M}_{2/n}\text{O} ; \text{Al}_2\text{O}_3 ; x \text{SiO}_2 ; y \text{H}_2\text{O}$ $\left\{ \begin{array}{l} * 2 \leq x < \infty \\ * \text{M} = \text{cation of valency } n \end{array} \right.$
Diameter of channel	2,2 to 8 Å
Diameter of cavity	6,6 to 11,8 Å
Internal surface	several hundreds of m^2/g
Internal porous volume	$0 < v_p \leq 0,4 \text{ cm}^3/\text{g}$
Cation exchange capacity	0 to 650 meq/100 g
Thermal stability	500 to 1000 °C

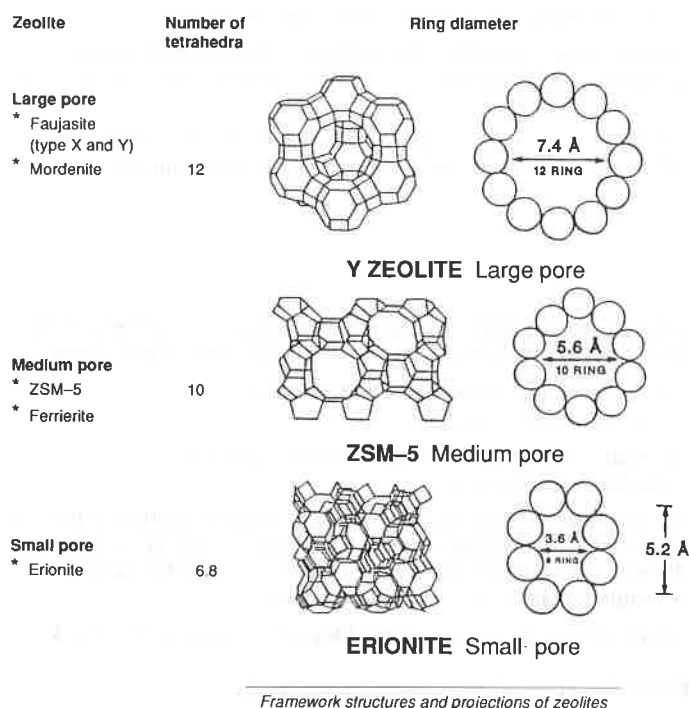
The central atom of the primary building block tetrahedron of the zeolite can be replaced by a large number of tri- or tetravalent atoms. For instance B, Fe, Ga, Ge, Ti and perhaps Cr, Zr and Hf can substitute for Si atoms. Consequently, the activity and the properties of the zeolite may be modified. The catalytic activity is in relationship with the acid centres situated on the intracrystalline surface.

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More than 150 synthetic zeolite types and 40 zeolite minerals are known. Natural zeolites (e.g. clinoptilolite, phillipsite, chabazite, etc.) are to be found in large quantities and high purities (> 90 %) in rocks of volcanic origin. They are ubiquitous in nearly every basalt formation. Synthesis of these materials was first attempted under those conditions under which they were presumed to have been naturally formed (at high temperature, high salt concentrations and under autogeneous pressures). This changed dramatically in 1949 when workers at Union Carbide synthesized zeolites by low temperature hydrothermal processes.

Today, most commercial zeolites are synthetic materials with high purities. The starting point is crystallization in autoclaves or open reactors from a more or less homogeneous gel obtained from a silica and an alumina source combined with water and high pH conditions (OH^-). The temperature is between 50-160 °C producing a pressure of less than 30 bars for a few minutes to a few days.



Three classes

FIGURE 3. - Commercially important synthetic zeolites used in catalytic applications.

Hence, the difficulty is to control the process in order to produce a reaction range where a single-phase, fully crystallized product may be isolated (figure 4). The initial metastable phase is transformed successively into one or more phases of higher stability according to the Ostwald law.

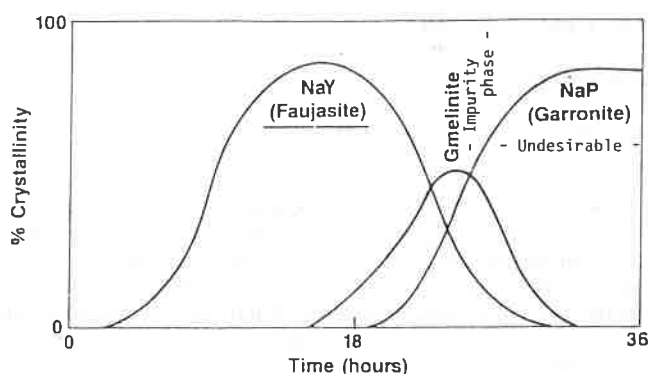


FIGURE 4. - A typical multiphase crystallization sequence, in this case for faujasite - a major catalyst component. The optimum product "window" has a short survival interval.

The yield of the zeolite synthesis is optimized by an induction period ("aging process") during which the reaction mixture is held near ambient temperature prior to raising the crystallization temperature. Small nuclei form during this phase.

In some cases, the synthesis may be performed in the presence of structure directing agents called templates, generally consisting in large organic cations like the tetramethylammonium (TMA) ion [2]. These templates have to be burned off the channels after crystallization.

After possible specific chemical reactions involving the framework atoms, the zeolite is well mixed with a binder, glue and/or diluent, and then pressed into beads, pills, tablets or extrudates to be used directly. Zeolites can also serve as a supporting structure for active compounds.

As all compounds related to silica, the dry zeolites are pulverulent and irritating for the respiratory system, but only those which crystallize as fibres (natrolite, erionite) are supposed dangerous (like asbestos).

Industrial applications of zeolites [3] [4] [5]

Major examples of zeolite uses will be reviewed successively in the following areas :

- Molecular sieves and drying agents.
- Ion exchangers :
 - applications in the nuclear industry,
 - environmental applications,
 - agriculture interest,
 - consumer applications,
 - medical and cosmetic uses.
- Catalysts :
 - applications in the petroleum industry,
 - use in organic chemistry.

Adsorption and molecular sieves

Separation of bulk hydrocarbons and linear paraffins

The linear paraffins that are produced as the desorbate are used for the manufacture of synthetic detergents while the raffinate is used as high-octan gasoline or low freezing point jet fuel.

Separation of aromatic in the liquid phase

Synthetic zeolites help to fractionate mixtures of liquids (Sorbex processes). It is difficult to separate aromatic isomers, such as xylenes and ethylbenzenes, by distillation (similar boiling points). Higher separation factors may be achieved in an adsorption system containing zeolites.

Separation of air

Production of oxygen and nitrogen (preferentially adsorbed) is carried out by pressure swing adsorption (PSA) over a zeolite adsorbent (5 Å or 13 X). It is largely used in small scale operations (domestic production of oxygen for asthmatic patients) in spite of its low energy efficiency.

Drying agents (general-purpose dessicants)

- Sealed cartridges of 3 Å, 4 Å and clinoptilolite are included in refrigeration circuits, vehicle braking (hydraulic brake systems of trucks and buses), air conditioning systems, transformers.
- Removal of moisture and/or organic vapours in sealed dual-pane windows. 4 Å zeolite mixed with silica gel.
- Protection of automobile exhaust systems from moisture and acid gases.
- Use in drying and purification plants.
- Hydrogen adsorption in fibre optic cables.

The optical fibres are kept in a substantially H₂-free environment by incorporating 0.2-15 Wt % of a Ag-exchanged zeolite into the water-blocking compound of the cable.

Use for gas purification [6a]

In natural gas treatment zeolites help to remove H₂S. General pollution control : mercury vapour, sulphur dioxide, nitrogen oxides (NO_x), etc.

Some examples of typical commercial applications are given in Table II.

TABLE II. - Operating principles of some commercially important zeolite molecular sieves [6].

Sieve Type	Application	Operating Molecule Sieving	Principles Polarity
3A	Drying of olefin-containing gas eg. cracked gas	Exclusion of olefins	High specificity for water
	Natural gas treatment (drying and removal of carbon dioxide)	Exclusion of hydrocarbons	High specificity for H ₂ O + CO ₂
5A	Separation of N-paraffins from petroleum fractions Separation of oxygen from air	Exclusion of isoparaffins and aromatics	specificity for nitrogen
13X	Sulphur removal from petroleum fractions		Specificity for mercaptans and sulphides

Gas storage systems

Zeolites can encapsulate gases at high pressures and elevated temperatures. When quenched at room temperature, the gases remain trapped and the system remains stable for very long periods of time. To obtain a quantitative desorption, the zeolite is destroyed by chemical dissolution or heated to a higher temperature. Possible storage of H₂, Ar, Kr, He, CH₄, etc.

- ⁸⁵Kr produced by nuclear fusion in light water reactors can be encapsulated into zeolites.
- ¹⁴C is released during the dissolution of space fuel as ¹⁴CO₂ which can be removed by selective adsorption on a molecular sieve.
- ¹²⁹I released as elemental iodine or organic iodides during fuel reprocessing can be separated and retained using silver-exchanged zeolites (which can be recycled).

Beverage carbonation/sprays

The considerable adsorption capacity of zeolites for carbon dioxide is utilized in a novel method for beverage carbonation at the time of use, rather than bottling under pressure. It also helps to preserve the ozone layer as CO₂ is used as the propellant gas in spray bottles.

Chemically loaded molecular sieves

The isolation of a reactive chemical or a catalyst is made possible by adsorption within the zeolite cavities until the time when it is needed for reaction (resin and rubber synthesis). Release is achieved by displacement with water or heating.

In other cases, the zeolite may be added to scavenge a by-product.

Gas chromatography

Use in gas/solid chromatography.

Ion exchange

Applications in the nuclear industry [7]

Long-term storage of long-lived hot radioisotopes (Cs⁺ and Sr⁺⁺) from nuclear plants fission by-products is achieved by drying the zeolite or clay-zeolite composites which are stable to ionizing radiation (cumulative radiation dose above 10¹⁰ rads) and have low solubility (in the pH domain 5-10.5), good dimensional stability and high selectivity (advantages over organic resin ion exchangers). At high temperature, the zeolite containing the radioisotopes can be converted to a glass (very low leach-rate).

At the time of the Three Miles Island accident, 2.3 kg of ¹³⁴Cs and ¹³⁷Cs as well as 0.3 kg of ⁹⁰Sr were fixed on a synthetic zeolite. Zeolites have also been used at Tchernobyl.

Isotopic enrichment

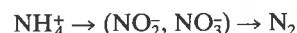
The preparation of curium 247 was reported by irradiation of lanthanide or trivalent actinide exchanged into X or Y zeolites.

Environmental applications

Improvement of mud filtrability and decanting

The removal and recovery of metals is possible with high selectivities for various metals (Pb²⁺, Cd²⁺, Ag⁺, Cu²⁺, Fe²⁺, Zn²⁺, Cr³⁺, etc.). It is mainly used in case of diffuse pollution with low concentration of toxic metals. The extraction of heavy metals is performed in bioreactors.

Waste water purification [8] by removal of ammonia and ammonium ions from aqueous effluents (clinoptilolite) with regeneration of the brines by biological processes :



Agricultural applications [9]

Soil Improvement

Zeolites exchanged with the nutrient ions ammonium (NH₄⁺) and potassium (K⁺) can be added to soils as ionic-type fertilizers with slow release in soils. Micronutrients, such as iron, copper, manganese and zinc, can be supplied by the zeolite. Relatively impure natural zeolites can be used.

- Additionally, the zeolite may function as a diluent in fertilizer mixtures and as an additive for improving physical properties of the soil.
- The observed growth and yield improvement of farm crops could result from the adsorption and retention of ammonia nitrogen and potassium, maintenance of water content and prevention of rott decay.

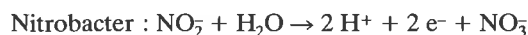
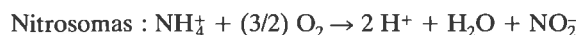
Stock-farming

- Zeolite minerals (clinoptilolite, zeolite A) added to the diets of pigs (5-6 % supplementation), chickens and ruminants in Japan have shown significant increases in gain of body weight per unit of feed. Also the presence of the zeolite in their diet contributed to the well-being of the animals with a considerable reduction of sickness and mortality. Dietary and antibiotic behaviour are not understood (reduction of NH₄⁺ by selective exchange ?).

Aquaculture and biotechnology

- Zeolites may be used as filters for water, fertilizers for aquarium plants and diet supply for fish.

• Removal of NH_4^+ from waste water by ion exchange. It is a simple fixation of NH_4^+ followed by a continuous biological regeneration. Two bacterial species are fixed on granulated clinoptilolite [10] :



Consumer applications

Laundry detergent builders [11] [12]

The principal divalent ions in water which are harmful in the laundry process are Ca and Mg.

• Zeolite A is a very effective insoluble ion exchange builder for removal of Ca^{2+} and zeolite X exchanges Mg^{2+} rapidly. In conjunction with other additives they can replace the sodium polyphosphates.

• The market is increasing rapidly (> 50 % phosphate-free washing powders in Germany) and the world production capacity of zeolite A amounts of 6,000,000 tons per year.

• Used zeolites can be regarded as non-hazardous materials following environmental tests.

Tooth paste abrasives

NaHA and CaHA hydrated powders, upon incorporation into a toothpaste formulation, provide effective abrasive action for teeth-cleaning. They are prepared from NaA and CaA by partial hydronium ion exchange with mineral acid to eliminate unwanted alkalinity.

Medical and cosmetic uses

Regeneration of artificial kidney dialysate solution using ion exchange capability (NH_4^+ selective).

Zeolite disinfecting agents

Ag^+ , Cu^{2+} and/or Zn^{2+} zeolite is a water and heat resistant bactericide especially effective in disinfecting drinking water.

Catalysts

This chapter is intended to demonstrate the numerous possibilities in which zeolites can be employed as catalysts in the petroleum industry and in organic chemistry.

Advantages of zeolites in heterogeneous catalysis

Zeolites are industrial heterogeneous catalysts which combine different properties (high acidity, shape selectivity and possible support for active components). Know how obtained from petrochemical processes on the catalytic properties of zeolites is being used nowadays for organic synthesis.

For instance, W. Hoelderich at BASF systematically investigated the use of zeolites for catalysing organic reaction and today holds more than 120 patents dealing with the synthesis of fine chemicals and their intermediates [13-18].

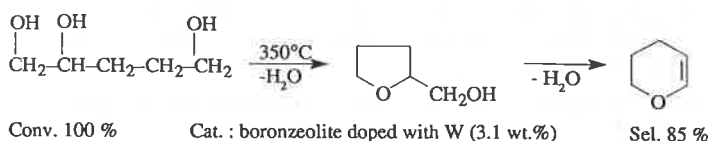
By suitable tailoring of these materials, one can combine a number of complex individual reactions into a "one pot" synthesis. Multifunctionality is a characteristic of heterogeneous catalysts which helps them to gain in importance [17].

After doping zeolites - either by ion exchange or by impregnation - with noble or heavy metals, it is now possible to combine dehydration and hydrogenation, isomerization and dehydrogenation or dehydration and rearrangement into a single process step.

Reactions involving several steps or multifunctional catalysis

e.g. : dehydration and rearrangement [19].

One reaction step instead of two and a higher yield of the rearrangement.



Another important capability of zeolite catalysis is their selectivity in comparison with classic synthetic pathways. Competing parallel reactions which usually lead to complex mixtures may be diminished or avoided. Basic advantages of zeolite type catalysts compared with conventional homogeneous systems are summarized in Table III.

TABLE III. - Advantages of heterogeneous over homogeneous systems.

Heterogeneous	Homogeneous
<ul style="list-style-type: none"> - Improved selectivity and high activity. - Easy separation of the catalyst from the reactive solution. - Possible thermal regeneration - No saline sewage. - Limited corrosion of the plant. 	<ul style="list-style-type: none"> - Competing consecutive or parallel reactions. - Complex mixture difficult to separate. - Low yield in end product.

Industrial catalytic applications [20]

The commercial use of zeolites as catalysts is a rather recent development (1959). The development of synthetic routes for manufacturing faujasite-type zeolites in big quantities led to their rapid introduction as cracking catalysts (Figure 5).

The major employment of zeolites is as acid cracking catalysts. The world consumption for this purpose is around 350.000 tons annually.

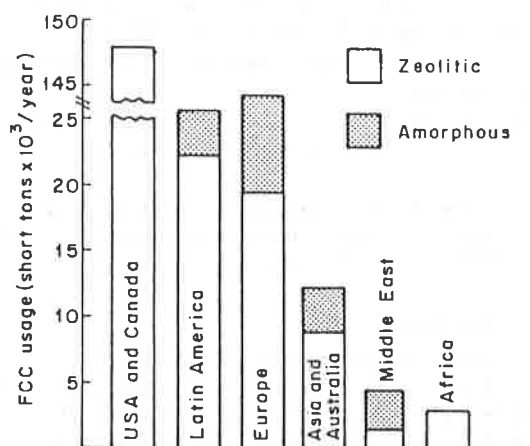


FIGURE 5. - Usage of FCC catalysts (D.E.W. Vaughan in R.P. Townsend ed.) (Properties and Applications of Zeolites, Chemical Society Special Publication, 1980, 33, p. 298).

Recent research efforts are directed toward the discovery and use of unique zeolites in the following areas :

- petroleum refining,
- production of synfuels,

- manufacture of petrochemicals,
- abatement of NO_x in industrial effluents.

Six properties make zeolites attractive as heterogeneous catalysts :

- well defined crystalline structure,
- high internal surface areas,
- uniform pores,
- good thermal stability,
- ability to adsorb and concentrate hydrocarbons,
- highly acidic sites when ion exchanged with protons.

Catalytic cracking of crude oils in a fluidized bed reactor (figure 6)

Preferred fluid cracking catalysts (FCC) are all faujasites able to increase the yield of gasoline range products, especially those with high octane ratings (high contents of olefines and aromatics).

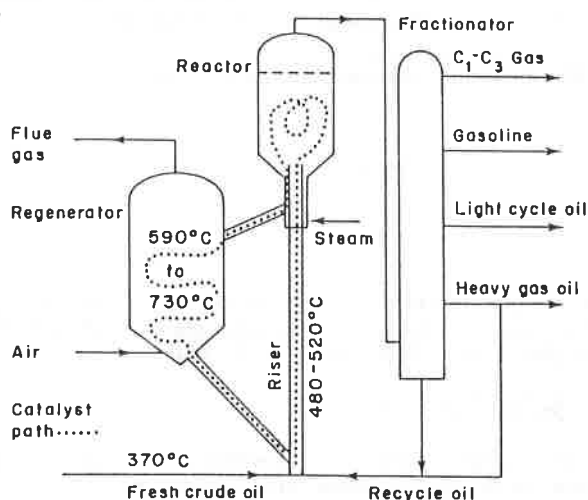


FIGURE 6. - Conventional layout of a fluidized bed cracking reactor and its associated processes (D.E.W. Vaughan in R.P. Townsend ed.) (Properties and Applications of Zeolites, Chemical Society Special Publication, 1980, 33, p. 301).

Hydrocracking

Heavy and residual gas oils are upgraded oil-heating, jet and diesel fuels and petrochemical feedstocks. High silica zeolites, such as synthetic faujasites, mordenite and erionite with a mixed metal composition (allowing hydrogenation-dehydrogenation properties), are used.

Selectoforming

N-paraffins from reformer product streams are selectively cracked (erionite, ZSM-5) to liquid propane gas which can be easily separated so eliminating low octane rating fractions from the product fuel. In this way the process increases the octane number.

Hydroisomerization or C5/C6 isomerization

Many refiners have been adding pentane and hexane isomerization capacity to meet the octane shortfall caused by the phase-out of tetraethyl lead in gasoline. A reduced Pt "large pore" mordenite is used.

Dewaxing

Long-chain linear and slightly branched paraffins have high melting points and adversely affect the cold flow properties of the oil (high pour points). ZSM-5 is used to selectively crack the long-chain linear paraffins to gasoline and LPG. This process can also make very high quality jet fuels, when combined with a subsequent hydrotreating step.

Benzene alkylation or ethyl benzene synthesis

This production is a vital stage towards the formation of styrene for polystyrene manufacture. The use of ZSM-5 eliminates the corrosion and waste disposal problems associated with the Friedel-Crafts reaction (AlCl_3 and BF_3 catalysts) and improves the reaction selectivity.

Xylene isomerization

It is the largest petrochemical application of zeolites (ZSM-5). The demand for p-xylene (used in polyester production) is larger than for o-xylene. p-xylene has a favoured diffusion rate in the zeolite crystal.

Production of synfuels

The methanol to gasoline (MTG) process of Mobil converts coal and natural gas to liquid fuels with intermediate methanol production using medium pore zeolites, such as ZSM-5 [21].

The zeolite catalyst used in MTG plants has the ability to convert oxygenated feeds to hydrocarbons and by a clever use of the time on stream other useful products can be collected. The basic process can be used to produce chemical feedstocks rather than fuels.

The chemical production from syngas and crudes are economic options for the future. e.g. : methanol to olefins (MTO) process. Union Carbide's MTO process with SAPO (silicoaluminophosphate) zeolite produces olefins in very high yields (> 90 %) and no aromatics.

Reduction of NO_x effluents

Selective catalytic reduction of NO and NO_2 using mordenite or Y-zeolites is a way to control NO_x emissions. In this process NH_3 is used as reducing agent to convert NO_x to N_2 and H_2O . Main applications are for power plants, nitric acid plants, and stationary gas and diesel engines. The zeolite-based catalysts are more efficient and less sensitive to contaminants than competing catalysts.

Synthesis of organic intermediates and speciality chemicals [13-18, 22, 23] (see Table IV)

This is a field for new applications of zeolites. The following list organic of reactions shows the potential interests and advantages of these catalysts for the chemical industry :

1. Electrophilic and nucleophilic aromatic substitutions.
Alkylation, acylation, halogenation, hydroxylation, nitration, hydrolysis, ammonolysis, etc.
2. Nucleophilic substitutions of aliphatic compounds.
Synthesis of amines, thiols, ethers and esters, etc.
3. Addition and elimination reactions.
Olefin hydration, additions of alcohols, thiols, amines.
Dehydration of alcohols, ethers, etc.
4. Isomerization reactions and rearrangements.
Isomerization of aromatics (xylenes, dihalogenobenzenes, etc.).
Isomerization of aliphatic compounds (olefins).
Rearrangements of compounds having functional groups (aldehyde, epoxide, ketone, etc.) : Beckmann, pinacolone, Wagner- Meerwein.
5. Hydrogenation (olefins) and dehydrogenation (alkanes) reactions.
6. Oxidation reactions.
Oxidation and epoxidations of olefins using hydrogen peroxide.
Partial oxidation of alkanes.
Hydroxylation of aromatics by H_2O_2 .
7. Condensation and cyclocondensation reactions.
Aldol condensation of aldehydes and ketones.
Diels-Alder cyclo-additions.
Building of aromatic heterocycles.

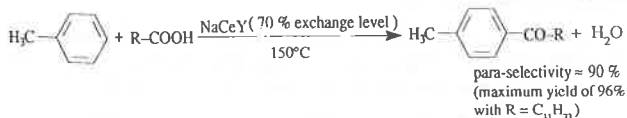
TABLE IV. - A Few Striking Examples of Synthesis

1. Friedel-Crafts acylations

Acylation of toluene

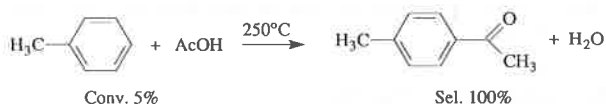
AlCl_3 is replaced by :

- a Ce-exchanged Y-zeolite [24]



In this case, the yield increases as the chain length of the acylation agent increases. No reaction is observed with $\text{R} = \text{Me}$.

- a HZSM-5 zeolite [25]



Acylation of heteroaromatics [26, 27]

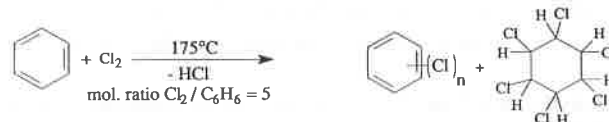
X	Conv. (%)	Catalyst	T (°C)	Sel. (%)
S	24	B-zeolite	250	99
O	23	Ce, B-zeolite	200	99
NH	41	Cs, B-zeolite	150	98

The use of Lewis-acids is avoided and thus contributing to the protection of the environment.

2. Halogenation

Chlorination of benzene

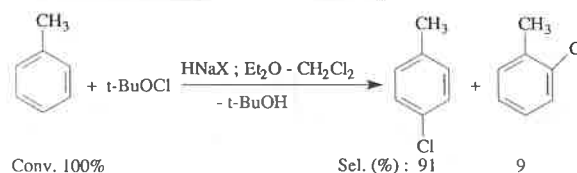
[28] (ionic substitution versus addition)



Conv. (%)	Catalyst	Selectivity (%)	
100	RE-Y *	97	3
98	NaHZSM-5	10	90

* RE-Y = rare earth exchanged Y-zeolite (faujasite).

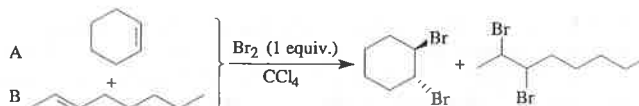
Chlorination of alkylated aromatics [29]



In the presence of the zeolite the p/o-isomer ratio is higher than when conventional Lewis acid catalysts such as FeCl_3 is employed (para 50 % ; ortho 50 %) [30].

Dibromination [31]

This example shows the possibility of shape selection between chemically similar functional groups.



System	Selectivities (%)		Comment
No zeolite (Z)	65	35	surface reaction pore shape selectivity
$[\text{Z} + (\text{A} + \text{B})] + \text{Br}_2$	96	4	
$(\text{Z} + \text{Br}_2) + (\text{A} + \text{B})$	17	83	

Zeolites in the chemical industry

From an industrial point of view, economic constraints play a major role in the choice of the reactions which can benefit from the use of zeolites.

For each member of a group of important organic intermediates the following aspects have to be accounted for to obtain the most appropriate estimate of the economical interests in a given synthesis :

- Raw materials available close to the plant,
- Possible use of a reaction sub-product which can be given some added value with possible destruction, separation and/or reuse of the other by-products. It can favour the creation of a new product line or strengthen the one this chemical belongs to,
- Simplification of an already existing synthetic route,
- Separation of a complex mixture made possible,
- Improvement of security and decrease of pollution hazards.

Conclusion

Shape selective acid catalysts will progressively make possible to improve and commercially exploit numerous economically interesting organic reactions. Limitations of homogeneous catalysts, environmental and process engineering problems occurring in the separation, work-up or possible recycling of those materials can be overcome by a possible change to heterogeneous catalysis.

Zeolites may contribute significantly to the reduction of raw material and energy costs and to the protection of the environment. Applications are just beginning, but new horizons are appearing rapidly.

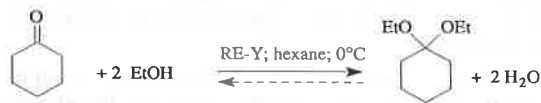
Miscellaneous

Environmental applications

Weather modification

Powdered dehydrated synthetic zeolites act as crystallization nuclei for water and water vapour.

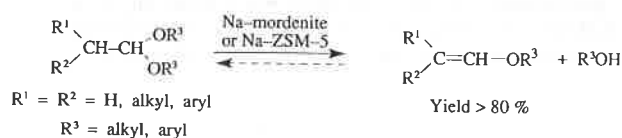
3. Acetalisation [32,33]



Water scavenger (3Å molecular sieve)	Yield (%)
Absence	30
Presence	100

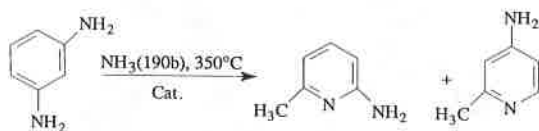
4. Elimination of alcohol [33, 34]

Synthesis of enol ethers by a C-O bond cleavage of acetals.



The zeolites are superior to the conventional homogeneous catalysts in both selectivity and lifetime. This possibility is an alternative route for the production of vinyl ethers (polymers) without starting from acetylene.

5. Benzamine rearrangement [35, 36]

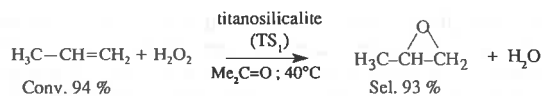


Conv. (%)	Catalyst	Sel. (%)
43	HZSM-5	83
29	SiO ₂ -Al ₂ O ₃	89
16	Al ₂ O ₃	57

* (mol. ratio H₃N/C₆H₄(NH₂)₂ = 60)

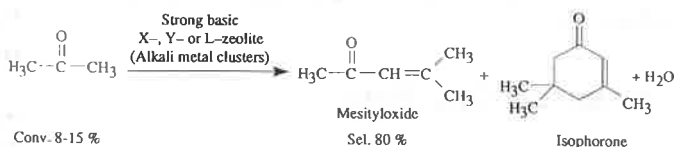
The zeolite demonstrates superior properties over other acid catalysts thus providing a useful new route for aminopyridines replacing the complicated Chichibabin reaction.

6. Epoxydation of olefins [37, 38]



A new synthetic route is combined with environmental advantages.

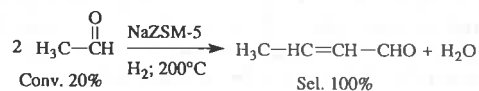
7. Aldol condensation [39-42]



The spatial limitations favour the formation of the less bulky mesityloxide.

The zeolite catalyst is superior to the more conventional α-Al₂O₃ (conversion 28 %, selectivity 44 %) and the product spectrum can be changed by manipulation of the catalyst's properties.

A patent by Mobil shows the possibility to obtain crotonaldehyde selectively from acetaldehyde in the presence of a common basic zeolite [43].



8. Heterogeneization of bimetallic catalytic systems

Very recently, the groupe of Professor Jacobs has published an elegant piece of work in which it is shown that both metals of the Wacker catalyst (Pd and Cu) can be exchanged on faujasite type zeolites with specific Si/Al framework ratios. The heterogeneized Wacker system catalyzes the oxidation of ethylene into acetaldehyde in exactly the same way as the homogeneous system [44].

Solar energy

Zeolite combined heating and cooling systems have also been developed. At ambient temperature a large quantity of water vapour is adsorbed and when heated most is desorbed even at high partial pressures. Zeolites are irradiated by the sun and water vapour is desorbed during the day, condensed and stored during the night. The heat of condensation is given to the external water loop (hot-water and space heating provided).

Oil pollution treatment

Adsorbant : zeolite + binding agent (methylsiloxane, tartaric acid, sodium bicarbonate).

Capacity : 0.7 g oil for 1 g zeolite.

Agricultural applications [9]

Stock-farming

Zeolite minerals are used to control malodor due to animal wastes. In poultry houses, ammonia and hydrogen sulfide levels can be greatly reduced.

Consumer applications

Flame extinguishers

A zeolite powder may function as a dry solid flame extinguisher by the following actions :

- blanketing effect by the release of an adsorbed gas like H₂O vapour or CO₂,
- production of a cooling effect (water vapour release),
- mechanical reduction of heat flow from the flame to the cold combustibles,
- release of a chemical flame inhibitor.

Electrical conductors

Mobile cations located in zeolite channels impart ionic electrical conductivity suitable for use in an electrostatic copying process.

Medical and cosmetic uses

Zeolite containing bases for topical pharmaceuticals

Topical pharmaceuticals (ointments, etc.) contain zeolite as base material to regulate the release of active ingredients and to prevent the volatility of the substances.

In-vivo imaging

Paramagnetic complexes (gadolinium hydrates) have been proposed for medical imaging examinations. Only a very small amount of material is needed for the three-dimensional imaging of the gastrointestinal tract with the following advantages : non-toxic, high sensibility, quick elimination, possibility to take as many pictures as necessary.

Body deodorant powder containing zeolites

Preparation by encapsulation of crystalline zeolite particles (e.g. Cu-exchanged A-type zeolite) with an inorganic compound (silicate, carbonate).

New research directions

New materials

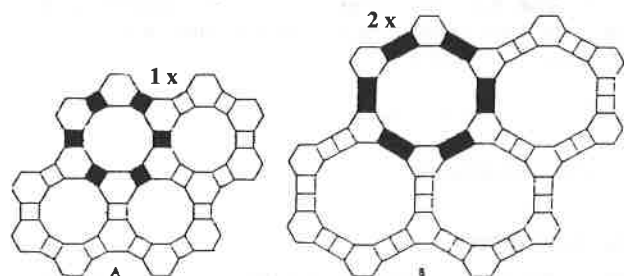
Silicates and aluminophosphates

During the last ten years, most of the work done in the field of new zeolitic materials synthesis has followed two main axes :

- New chemical composition of known structures ; for example : ZSM-5 with B, Ga, Fe [45], Ti [46, 47], Ge [48] in tetrahedral substitution for Si.

- New structures, essentially based upon the aluminophosphate framework.

One of the main issues in this point is to find a structure with a channel opening larger than the 7.4 Å of the faujasite family. This has been done recently (Figure 7) with the discovery of the VPI-5-aluminophosphate [49, 50]. Even if this is a major discovery in the field of new materials, it must not be forgotten that the already known MCM-9 could be considered as a structural analog of the VPI-5 in the silico-aluminate family. Moreover, R. Szostak at the Georgia Institute of Technology has demonstrated that VPI-5 and H1, discovered by D'Yvoire in 1961 were structural analogs. More recently an ultralarge pore gallium-phosphate material called cloverite by their inventors, H. Kessler of the CNRS, Laboratoire de Matériaux Minéraux in Mulhouse (France), and C. Baerlocher of the Swiss Federal Institute of Technology (ETHZ) in Zurich, has been discovered [51].



Aluminum-phosphorus-oxygen frameworks (AlPO₄)

AlPO₄-5
Union Carbide
E.M. Flanigen
1983
(12 ring)

VPI-5
Virginia Polytechnic Institute
Mark Davis
1987
(18 ring)
Excellent thermal stability has been reported.
First molecular sieve with pores larger than 10 Å.

FIGURE 7. - New Zeolites : The example of the aluminophosphate family.

Only a few structures are fully determined.

In the large family of the microporous solids [52] many new compounds have been developed.

The two main directions, which have been worked out are in the following order of importance :

- Opening of lamellar structures, whose most [53] [54] representative compounds are pillared clays. They offer the same versatility as zeolites do with a somewhat bigger opening (9 Å and more) and the more pronounced possibility to heterogenize homogeneous catalysis.

- Synthesis of microporous aggregates [55] offering a completely different matrix chemical composition, which can be adapted to the specific need of the application by the usual chemical modification of amphoteric oxides.

These materials could offer an alternative to zeolites in some specific applications.

New approaches to the properties of zeolites : use of computers

Today, spectacular advances are also being made in the use of theoretical calculations to produce computer graphics [56] [57] of zeolite structures and to study their properties (Figure 8).

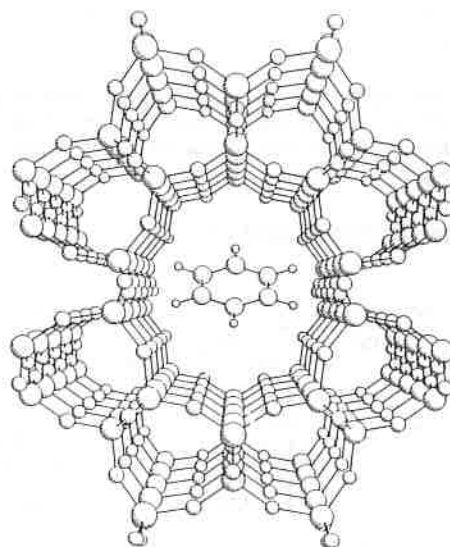


FIGURE 8. - The computer-generated graphic of a benzene molecule sorbed in the channel of zeolite Theta. 1. B.P.

These modelling techniques (for a few years largely used as protein structure predictions) have a wide range of applications which include : cation distributions, acid strengths of catalytic sites, intergrowth phenomena, derivation of new structures, molecular adsorption and selective diffusion of organic molecules through zeolite frameworks. This new instrument will help in finding new structures and their relationships with the ones that are already known.

Another new area of research which has interesting prospects is the investigation of the zeolites unusual electronic properties.

Zeolites as molecular electronic materials

Though still at a fairly early stage those studies may well quickly offer a wide range of new applications [58, 59] as suggested below.

Intrazeolite semiconductors

Microscopic particles (5-100 Å) of peculiar electrical, optical and magnetic properties can be included in zeolite matrices (large crystals) with a very uniform size distribution. After incorporation CdS, CdSe and ZnS semiconductor clusters present

interesting optical properties for potential photocatalysis or photoconversion applications. Sodalites (β -cages) encapsulating silver anions have also been prepared with photo-optical characteristics for high resolution imaging and data storage. Selenium chains stabilized in various zeolite channels show photoconductivity with possible use in photoelectric devices and xerography.

Conducting polymers in zeolites

Conducting and semiconducting chain structures (polythiazyl, polypyrrole and polyaniline) can be encapsulated in zeolite channels to form "isolated" 1D conducting chains.

Intrazeolite electron-transfer chains

Redox active molecules can be introduced within a zeolite framework and serve as models for photosynthetic chains and energy conversion systems.

Zeolite electrodes

After appropriate modifications of their composition, zeolites can be used as part of electrode systems of high product selectivities or as matrix for the electrode components. They may be used as solid electrolytes in ion-selective electrodes and as cathode materials in batteries.

Zeolite batteries

Solid state multiple-layer batteries with excellent operating characteristics have been built. They are based on the ionic conduction (cation mobility) and thermal stability (500 °C) of zeolites.

NH_4^+ and H_3O^+ zeolites A, X or Y with Pt electrodes show possible fuel cell applications.

Chemical sensors

Zeolites may be used as size and shape selective chemical sensors. Their potential applications range from moisture sensing, oxygen monitoring, carbon monoxide detection to the selective detection of gas like ethylene, ethane, etc. The optical properties of intrazeolite luminescent metal probes (like Eu^{3+} , Mn^{2+} , Ag^+ , etc.), the change of the dielectric constant [60] of the zeolite (Pt doped), etc. are used.

Zeolites as non-linear optical materials

Organic molecules (p-nitroaniline, etc.) can be confined in an acentric zeolite host (AIPO-5) to get non-linear optical (NLO) effects.

Zeolite membranes and thin films

The major use of these microstructures offering a controlled porosity in the 10 Å range is in chemical sensors as "molecular sieve" elements.

Only those molecules which are able to go through the membrane will be detected at the sensor surface. The zeolite crystals are incorporated in a glass or ceramic matrix of which the synthesis derives from sol-gel technology. Thin composite coatings can also be produced by electrodeposition methods.

Zeolite catalysts as inorganic mimics of enzymes

Publications are beginning to appear which indicate the importance of zeolite catalysts in stereochemistry.

New development in the fields of phosphates, clays, etc. will offer the possibility to combine catalytic properties and shape selectivity.

The silicon-based zeolite frameworks may replace the 3D protein portion of natural enzymes with which they have a number of striking structural similarities [61]. Some new revolutionary cata-

lysts may be found combining the features of metalloenzymes and metal-ion-containing zeolites as mentioned below :

- Metal phthalocyanine complexes can be trapped in faujasite supercages which still retain their shape selectivity. Substrate selectivity has been demonstrated by this new catalyst which also exhibits regioselectivity and stereoselectivity. This opens up the possibility to steer organic reactions, such as partial oxidations, in a particular direction less favoured when a homogeneous catalyst is employed.

- The iron proteins hemoglobin and myoglobin.

A synthetic mimic, a cobalt-salen complex inside a zeolite Y supercage, shows a remarkable stability toward autoxidation and negative co-operativity.

- The cytochrome P450

Cytochrome P450 are monooxygenase enzymes which have the unique ability to convert, for example, unactivated alkanes to alcohols with high selectivities. Numerous models of the heme-iron active site of these enzymes have been designed and one of them which consists of a Fe/Pd/A zeolite compares favourably with the selectivity of the natural systems.

All these advances will enable scientists to proceed further along the road leading to enzyme type catalysis, the most subtle form of shape selectivity.

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