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From Zeolite to Host-Guest Nanocomposite Materials

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1. Introduction

In nature, zeolites as aluminosilicate members of the family of microporous solids are often formed where volcanic rock of specific chemical composition is immersed in water so as to leach away some of the components. Zeolites are known as "molecular sieves". They have many useful applications such as: ion exchange technology, filtering, odor removal, chemical sieve and gas absorption tasks but the most well known use for zeolites is in water filtration applications. In a typical example, Figure 1 presents a cubic structure of zeolite Y with 3D system of channels.

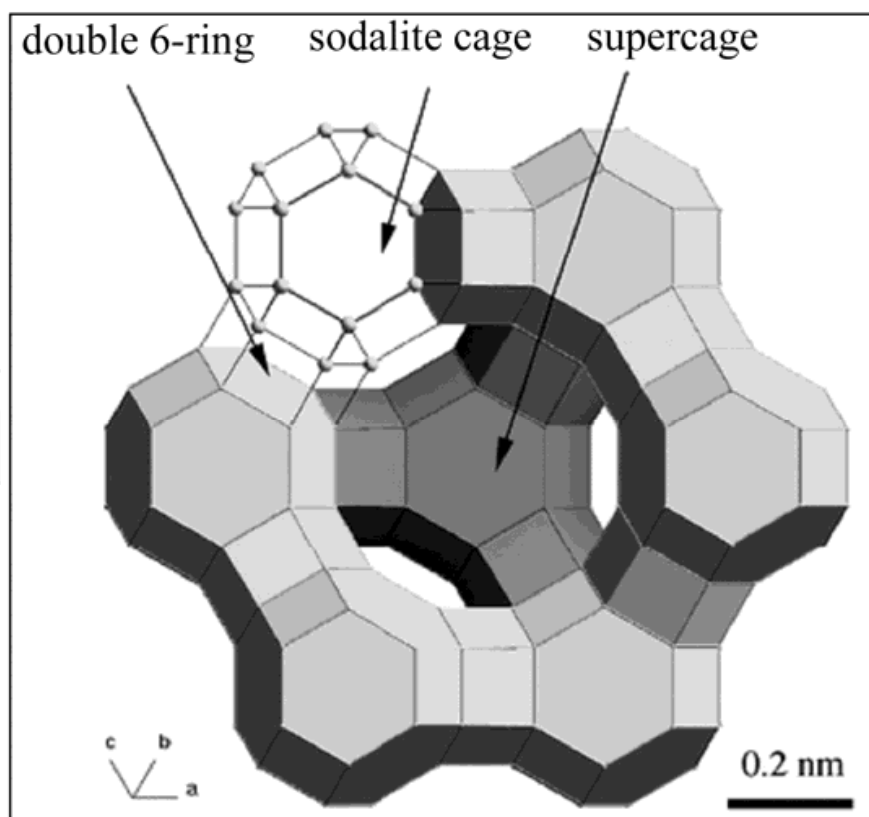
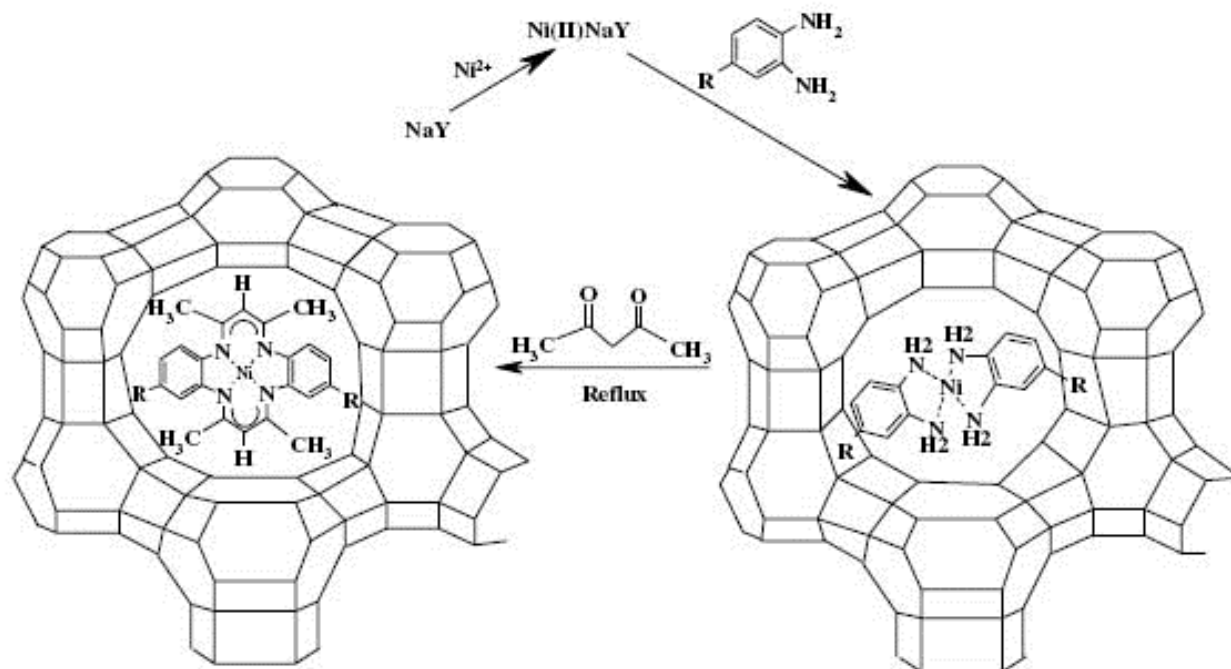


Fig. 1. The structure of zeolite Y.

Due to the uniformity of the pore dimensions, zeolites can act as "host materials" for other molecules. Only molecules of certain size are able to be absorbed by a given zeolite material, or pass through its pores, while molecules of bigger size cannot. During the last two decades, zeolites with nanoscale dimensions open a new view in host (nanopores of zeolite)-guest (transition metal complex) nanocomposite materials. The encapsulation of transition metal complexes into the framework sites of the molecular sieve has attracted considerable attentions as the preparation of novel catalysts, owing to which possess the advantages of both homogeneous catalysis as the metal ion in the solution and heterogeneous catalysis as the molecular sieve in the polyphase system. So that, the catalytic efficiency of zeolite encapsulated metal complexes (ZEMC) is much higher than that of the neat complexes and the ZEMC nanocomposites have provided the opportunity to develop catalytic process for the selective oxidation, alkylation, dehydrogenation, cyclization, amination, acylation, isomerisation and rearrangement of various substrates and are able to produce intermediates as well as most industrial.

Basically, there are three main approaches to encapsulate complexes: the zeolite synthesis (ZS), the flexible ligand (FL) and ship-in-a-bottle methods. In the ZS method, transition metal complexes, which are stable under the conditions of zeolite synthesis (high pH and elevated temperature), are included in the synthesis mixture. The resulting zeolite encapsulates the transition metal complex in its voids but in the FL method, a flexible ligand is able to diffuse freely through the zeolite pores. Scheme 1 shows a typical "flexible ligand" synthesis of zeolite-Y encapsulated metal complexes of Ni(II).



Scheme 1. "Flexible ligand" synthesis of zeolite-Y encapsulated metal complexes of Ni(II).

To ensure encapsulation, FT-IR, UV-Vis spectroscopy, powder X-ray diffraction patterns (XRD) and BET (Brunauer-Emmett-Teller) technique can be applied.

The investigation of reported results reveals that zeolites encapsulated metal complex as heterogeneous catalysts make higher selectivity and conversion percentage than that of the homogeneous catalysts.

2. Host molecules

The long history "host-guest" or "supramolecular" chemistry has come to the fore front in contemporary researches with the awarding of the 1987 Nobel Prize in chemistry to Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen. In molecular engineering, host-guest chemistry describes compounds that are composed of two or more molecules or ions that are held together in unique structural relationships by forces other than those of full covalent bonds. Host-guest chemistry encompasses the idea of molecular recognition and interactions through noncovalent bonding (hydrogen bonds, ionic bonds, van der Waals forces, and hydrophobic interactions). Although supramolecular systems are often held together by weaker interactions than covalent systems, in some cases the "strength" of supramolecular systems actually lies in the weakness of these intermolecular forces. In particular, the weakness of these interactions allows host-guest binding to become a reversible process, so that a host and guest can associate and dissociate without either of the building blocks being damaged or altered. This can be useful for systems such as molecular switches and for catalysis, and is utilized frequently in natural enzymes. Macrocyclic hosts are molecular receptors that are arranged as a ring, in which the guest, or substrate, may bind in the interior. Macrocyclic hosts can be generally classified as types of "endoreceptors", in that they bind with their guests located in the interior of the host [1]. "Exoreceptors", in contrast, bind to substrates on their exterior. Some common examples of macrocyclic hosts include:

- Cyclodextrins
- Calixarenes
- Cucurbiturils
- Crown ethers
- Cryptophanes
- Porphyrins
- Cyclotriveratrylenes
- Carcerands
- Zeolites

2.1 Cyclodextrins (CDs)

In 1891, cyclodextrin molecules made up of cyclic oligosaccharides containing α -(1,4)-linked glucopyranosyl units were described by A. Villiers [2]. Typical cyclodextrins contain a number of glucose monomers ranging from six to eight units in a ring, creating a cone shape. Thus denoting:

- α -cyclodextrin: six membered sugar ring molecule
- β -cyclodextrin: seven sugar ring molecule
- γ -cyclodextrin: eight sugar ring molecule

Chemical structure of the three main types of cyclodextrins is shown in Fig. 1.

The production of cyclodextrins (CDs) involves treatment of ordinary starch with a set of easily available enzymes [3]. Several synthetic methods for the preparation of glycosylated cyclodextrins have been reported [4, 5]. Recently, β -cyclodextrin and hydroxy propyl β -cyclodextrin spheres with a particle size less than 400 nm were prepared by Mammucari and co-workers via an Aerosol Solvent Extraction System (ASES) process [6].

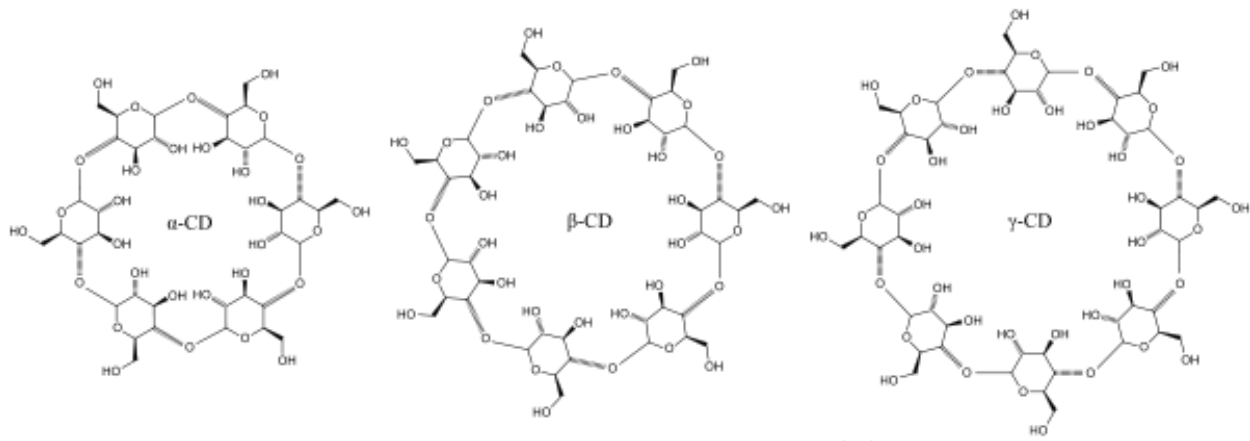


Fig. 1a. Chemical structure of cyclodextrins.

As a class of water-soluble and nontoxic cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic interior, CDs have been extensively investigated in host-guest chemistry. One of the most important properties of CDs is the inclusion of guest molecules into their cavities. The cavity size of CDs increases with the increasing number of glucopyranose repeating units. The cavity diameter of CDs is about 0.44 - 0.83 nm (α -CD: 0.49 nm, β -CD: 0.62 nm, γ -CD: 0.80 nm) [7, 8]. Furthermore, recent novel approaches to chemical sensing systems using supramolecular structures such as CD dimers, trimers and cooperative binding systems of CDs with the other supramoleculars have been mentioned [9]. When a competitive guest is added to the aqueous solution of fluorophore-CD, the fluorophore is excluded from the inside to the outside of the CD cavity. The fluorescent CD exhibits strong emission in the self-inclusion state due to the hydrophobic environment of the CD cavity and exclusion of the fluorophore from the cavity to bulk aqueous media weakens its fluorescence intensity. Therefore, fluorescence intensity of many kinds of "turn-off" fluorescent chemical sensors decreases by complexation with guest molecules. On the other hand, in "turn-on" fluorescent chemical sensors by inclusion of a hydrophobic guest molecule into the cavity of the fluorophore-CD conjugate, the fluorophore is located in a more hydrophobic environment, thus the fluorescence intensity increases (Fig. 2a and 2b).

CDs can be used as modified surface agent in the synthesis of nanostructure materials. Zhao and Chen have synthesized multi-petals ZnO nano-structure in the presence of β -cyclodextrin and they found that if not using β -CD in the preparation process, only larger rods could be obtained [10] and according to recent report, β -Cyclodextrin (β -CD)-functionalized CdSe/ZnS quantum dots (QDs) apply for optical sensing [11]. To develop functional nanoweb, Uyar et al. have synthesized cyclodextrin functionalized polyethylene oxide (PEO) nanofibers (PEO/CD) [12]. Additionally, CDs are also used for filtration purposes [13-15]. Cyclodextrin-capped nanoparticles can apply in catalyst industry. Fig. 3 represents TEM images of α -Cyclodextrin capped Au nanoparticles [16].

Other important applications of CDs involve: supramolecular carrier in organometallic reactions [17] and pharmaceutical applications for drug release [18,19]. To produce HPLC columns allowing chiral enantiomers separation, β -cyclodextrins are used [20].

2.2 Calixarenes

Calixarenes as macrocycles or cyclic oligomers are based on a hydroxyalkylation product of a phenol and an aldehyde [21]. These macromolecules have hydrophobic cavities that can

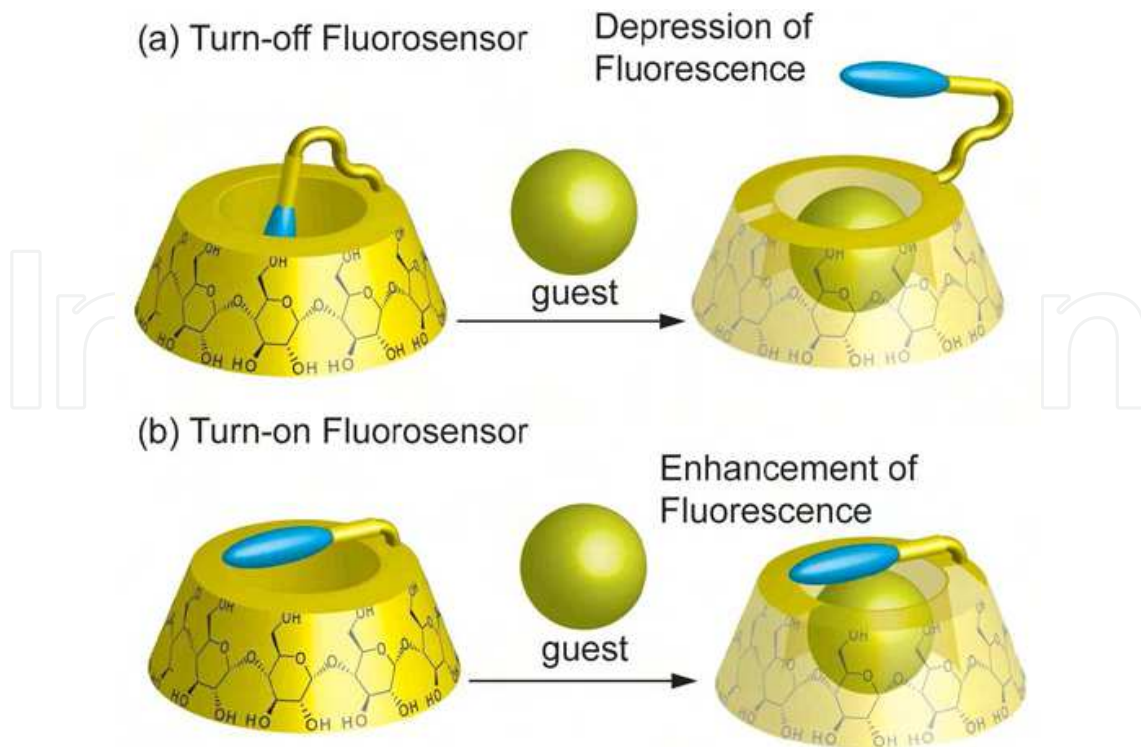


Fig. 2. (a) Turn-off and (b) Turn-on fluorosensors [9].

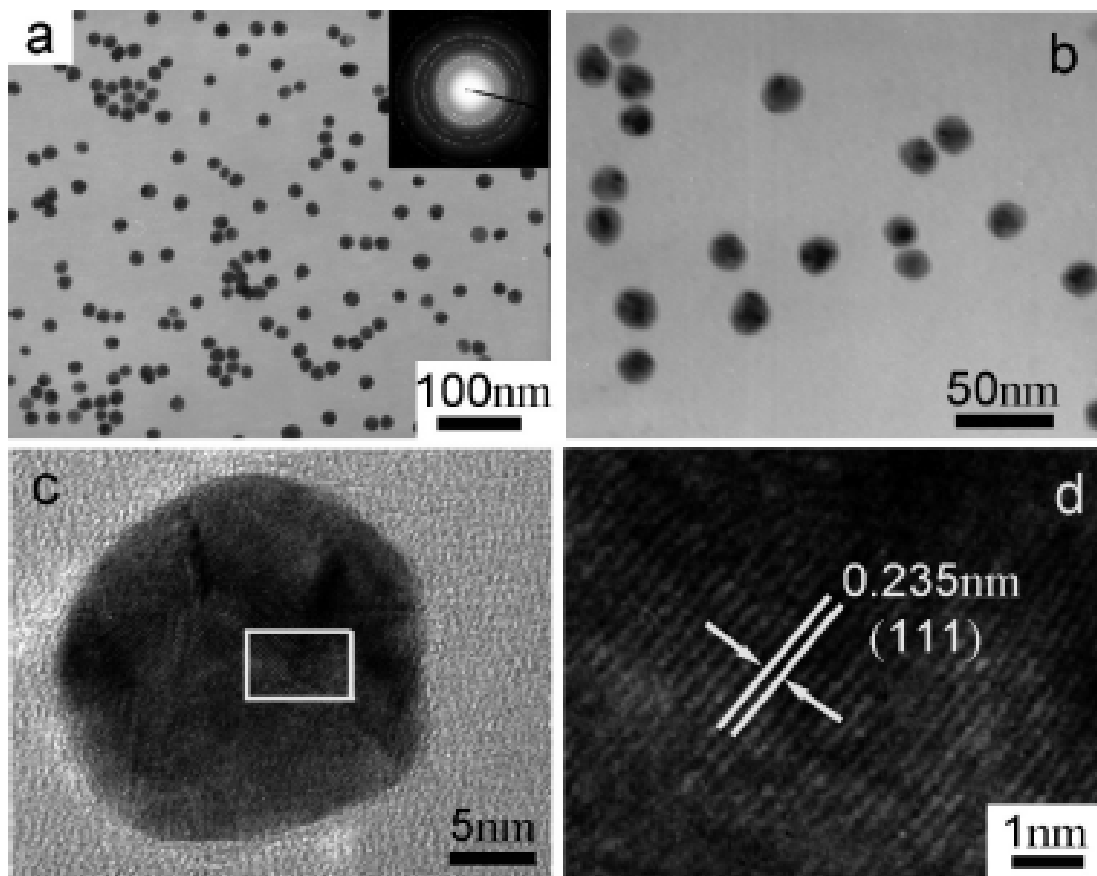


Fig. 3. TEM (a,b) and HRTEM (c,d) images of α -Cyclodextrin capped Au nanoparticles [16].

hold smaller molecules or ions and belong to the class of cavitands known in host-guest chemistry. Like cyclodextrins, these scaffolds are able to bind hydrophobic organic molecules and can be modified with carbohydrate ligands on one face of the molecule with control over ligand to ligand spacing. The general structure of calixarenes represents in Fig.4.

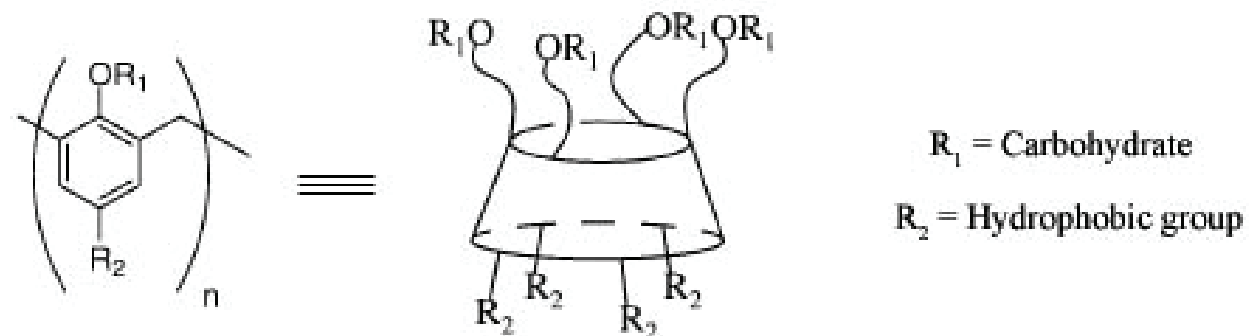


Fig. 4. The general structure of calixarenes.

These conjugates have been useful for both site-directed drug delivery [22] and for studies of water-monolayer surface interactions [23]. Calixarenes are efficient sodium ionophores and are applied as such in chemical sensors. On the other hand, these molecules exhibit great selectivity towards other cations. Calixarenes are used in commercial applications as sodium selective electrodes for the measurement of sodium levels in blood. In this case, Jin reported several new fluorescent Na^+ sensors based on calixarenes (Fig.5) [24]. Use of different types of calixarenes as sensitive layers reveals wide possibilities in control of sensitivity and selectivity of sensors [25, 26].

Ludwing and Dzung have discussed about molecular design principles of calixarene-type macrocycles for ion recognition and the relationship between their structure and selectivity [27]. Calixarenes as excellent surfactants have a remarkable capacity for molecular encapsulation, are also proficient at encapsulating nanoparticles. Therefore, these compounds can be used to control the growth of nanomaterials because of their stable cyclic structure in spite of low molecular weight and also very favorable properties for use as high-resolution resists [28]. Wei reported the synthesis of Au and Co nanoparticles by using C-undecylcalix[4]-resorcinarene (C11 resorcinarene), as shown in Fig. 6 [29].

Calixarene derivatives such as *p*-sulfonato-calix[*n*]arenes can form host-guest inclusion complexes in a similar way to cyclodextrins. Such water soluble calixarenes display interesting biological properties such as antiviral and anti-bacterial activity [30]. It is found that calixarene derivatives as resist materials are used for electron-beam lithography [31, 32].

2.3 Cucurbiturils (CBs)

A cucurbituril is a macrocyclic molecule consisting of several glycoluril [$=\text{C}_4\text{H}_2\text{N}_4\text{O}_2=$] repeat units, each joined to the next one by two methylene [$-\text{CH}_2-$] bridges to form a closed band. The oxygen atoms are located along the edges of the band and are tilted inwards, forming a partly enclosed cavity. Cucurbiturils were first synthesized in 1905 by Behrend, by condensing glycoluril with formaldehyde in concentrated sulfuric acid at a fairly high temperature ($>110^\circ\text{C}$) [33], but their structure was not elucidated until 1981 [34]. Cucurbiturils are commonly written as cucurbit[*n*]uril, where *n* is the number of repeat units ($n=5,6,7,8$ and 10). A common abbreviation is CB[*n*]. Fig. 7 and Fig. 8 show X-ray crystal structures of CB[*n*] ($n=5-8$) and synthetic method of CB[6], respectively [35, 36].

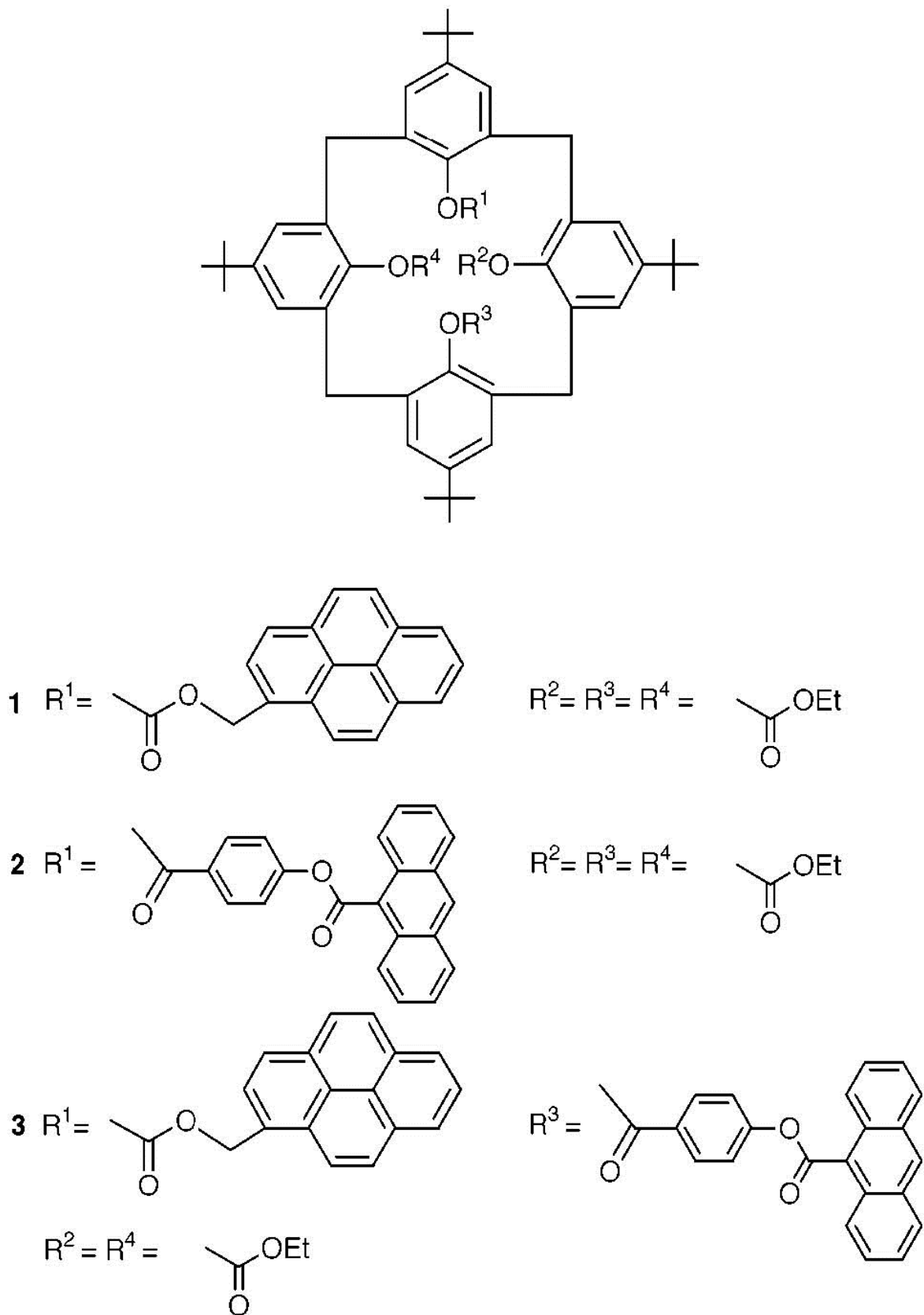


Fig. 5. New fluorescent Na^+ sensors based on Calixarenes [24].

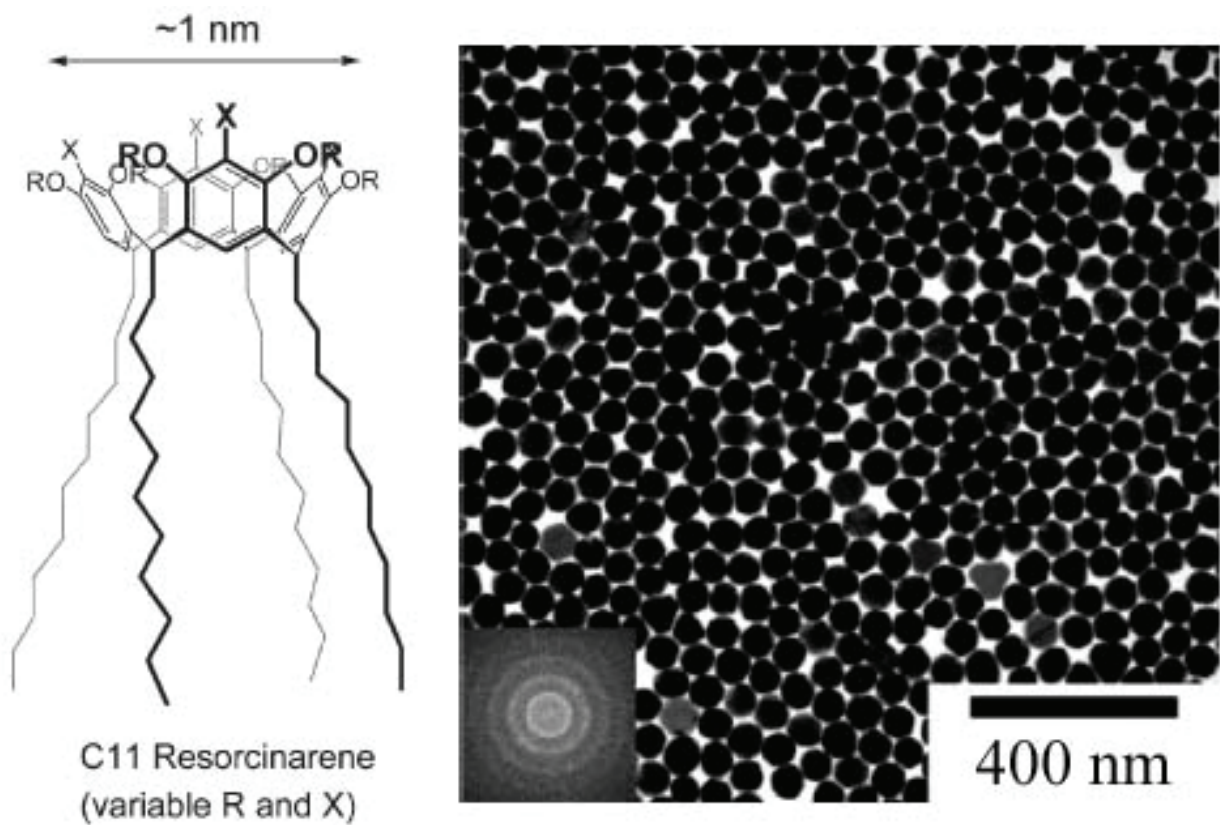


Fig. 6. TEM image of Au nanoparticles prepared by using C-undecylcalix[4]-resorcinarene (C11 resorcinarene) [29].

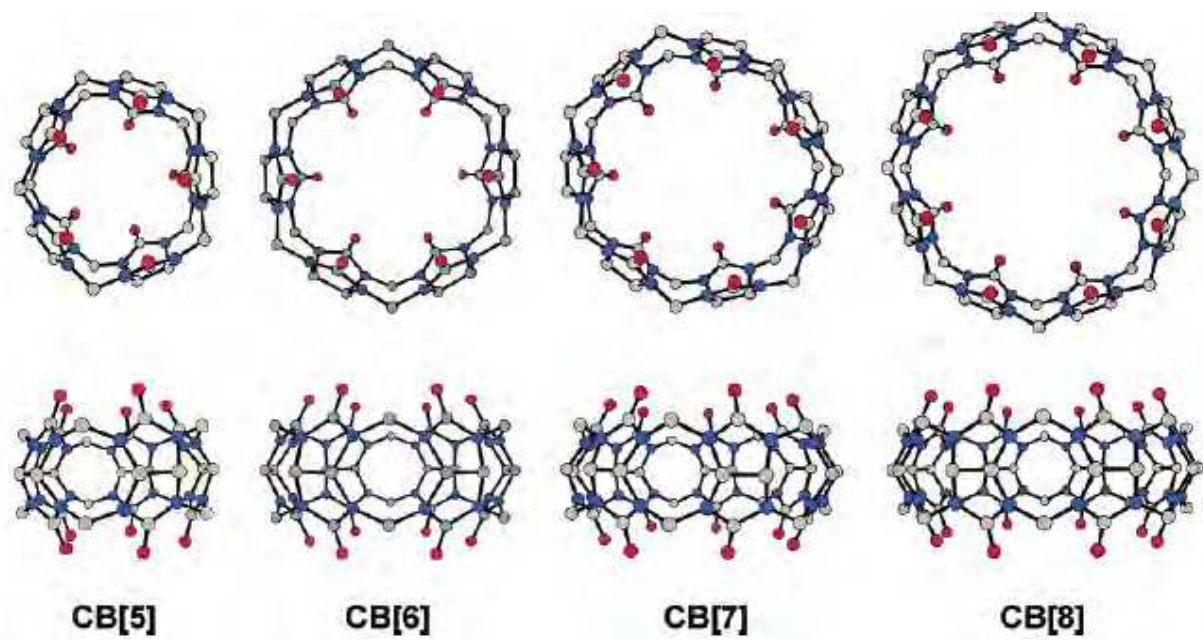


Fig. 7. X-ray crystal structures of CB[*n*] (*n* = 5-8). Color codes: carbon, gray; nitrogen, blue; oxygen, red [35].

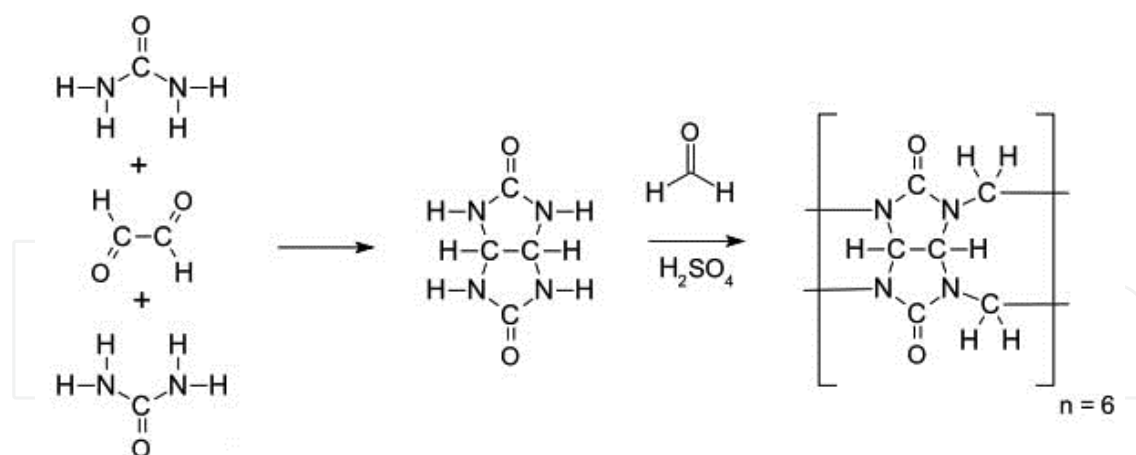


Fig. 8. Synthetic method of CB[6] [36].

The cucurbiturils are often compared to cyclodextrins (Table 1), which are considered to be their closest relatives in terms of size and shape, and the fact that both are often studied in aqueous solution [37].

Host	Portal Diameter (Å)	Interior Cavity Diameter (Å)	Height (Å)	Cavity Volume (Å ³)	Solubility in Water (Mm)
CB[5]	2.4	4.4	9.1	82	20-30
CB[6]	3.9	5.8	9.1	164	0.018
CB[7]	5.4	7.3	9.1	279	20-30
CB[8]	6.9	8.8	9.1	479	<0.01
CB[10]	9.5-10.6	11.3-12.4	9.1	870	Not reported
α -CD	4.7	5.3	7.9	174	297
β -CD	6.0	6.5	7.9	262	16
γ -CD	7.5	8.3	7.9	427	293

Table 1. Cavity dimensions and aqueous solubilities of CB[*n*] and CD host [37].

The cavity size of CB[6] as the first member of the CB[*n*] family is approximately the same as that of α -CD, and both hosts have hydrophobic cavities. As a result, binding involving CB[6] can be more selective compared to binding involving the more flexible α -CD host. Cucurbiturils have been shown to have a variety of potential applications. The ability of CB[*n*] to act as a catalyst for a chemical reaction was recognized by Mock relatively soon after his characterization of CB[6] [38, 39]. He realized that, since CB[6] has two electron rich portals, it had the potential to bring two cationic reactants in close proximity, as well as in specific orientations, so that the two reactants could undergo an accelerated reaction if they were simultaneously bound with the macrocycle. The larger macrocycles, such as CB[7] and especially CB[8], have seen further use for catalyzing and inhibiting reactions, as their larger cavity size allow them to form complexes, including ternary complexes, with a greater variety of guests. Considerable interest has been devoted to the use of cucurbiturils as drug delivery vehicles. As mentioned in the discussion of CB[7], Day [40-42] as well as Kim [43] have studied complexation between CB[7] and platinum-based anti-cancer drugs. Kim and co-workers have recently explored the use of nanoparticles based on functionalized CB[6] as drug delivery vehicles [44, 45]. Also, depending on the situation, they may also improve the solubility of a drug [46], reduce its undesired toxicity [47], improve its stability or activate

the drug [48]. In many cases the complexation between cucurbituril and a guest causes a change in the guest's spectroscopic properties. While this is useful for measuring the complexation between the host and guest, it can also have applications towards detecting the presence of a particular compound that the cucurbituril has an affinity for. Recent developments in the use of cucurbiturils as biosensors has been shown by Nau and co-workers, to detect enzymes such as amino acid decarboxylases [49, 50]. On the other hand, the effects of CB[7] on the activity of proteases have been studied [51].

It is reported that the most photosensitizer dyes aggregate easily and have poor solubility in aqueous solutions. To overcome these limitations, there have been several approaches such as combination of photosensitizers with polymers or macrocycles. Because of water-soluble cyclic oligomers of glycoluril units linked by methylene bridges in cucurbiturils, CBs have emerged as versatile cyclic hosts that can form strong inclusion complexes with positively charged organic guests [52]. Additional above mentioned applications, CBs as organic capsules would be suitable hosts to improve the stability and solubility of gold nanoparticles in common solvents. Because a general problem of metal nanoparticles is their tendency to undergo agglomeration, which increases their particle size, and therefore, dramatically reduces the catalytic activity. Two general strategies have been developed to stabilize the particle size of the metal; 1) supporting the metal nanoparticles on suitable solid surfaces and 2) by using suitable ligands [53-56]. Therefore, CB[n] macrocycles can be used to stabilize the metal nanoparticles. Corma and co-workers have shown that the size of metal nanoparticles can be controlled by encapsulation in CB[7], which shows unprecedented behavior at stabilizing very small gold nanoparticles [57]. TEM images of gold nanoparticles obtained in the presence and absence of CB are shown in Fig. 9.

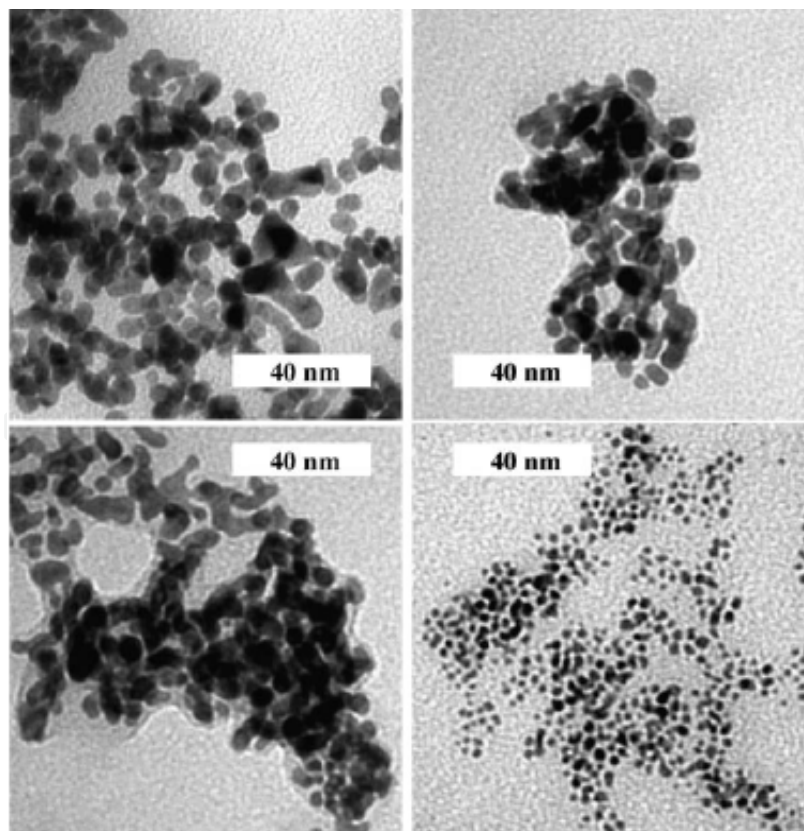


Fig. 9. TEM images of gold nanoparticles obtained in the absence of CB (top, left) and in the presence of CB[5] (top, right), CB[6] (bottom, left), and CB[7] (bottom, right) [57].

2.4 Crown ethers

In 1967, Charles Pedersen discovered a simple method of synthesizing a crown ether when he was trying to prepare a complexing agent for divalent cations [58, 59]. His strategy entailed linking two catechol groups through one hydroxyl on each molecule. This linking defines a polydentate ligand that could partially envelop the cation and, by ionization of the phenolic hydroxyls, neutralize the bound dication. He was surprised to isolate a by-product that strongly complexed potassium cation. He realized that the cyclic polyethers represented a new class of complexing agents that were capable of binding alkali metal cations. He proceeded to report systematic studies of the synthesis and binding properties of crown ethers in a seminal series of papers. The fields of organic synthesis, phase transfer catalysts, and other emerging disciplines benefited from the discovery of crown ethers. Pedersen shared the 1987 Nobel Prize in Chemistry for the discovery of crown ethers.

Crown ethers are named as x-crown-y where x denotes the total number of atoms in the cyclic backbone and y denotes the number of oxygen atoms (Fig. 10).

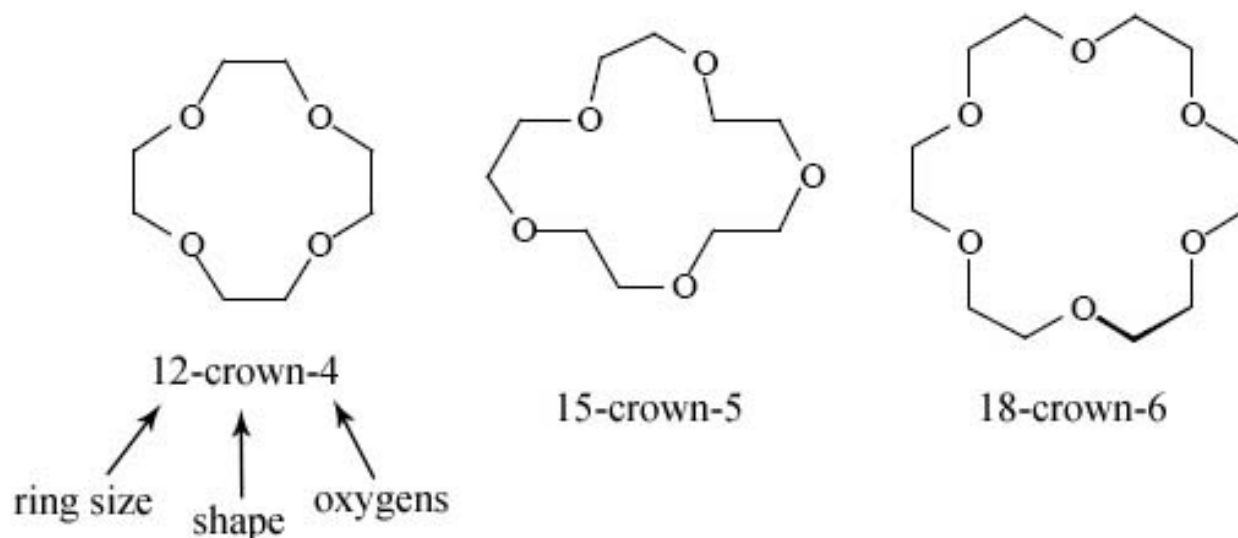


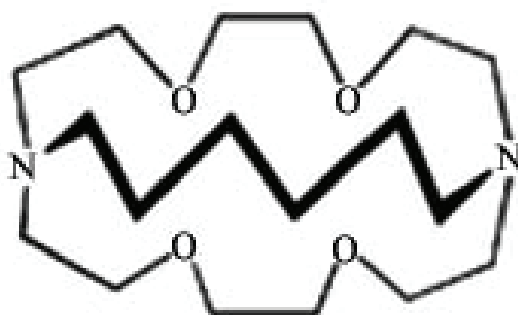
Fig. 10. General structure of crown ethers.

Crown ethers may be used to vary the solubility of the metal salts in non-polar and dipolar aprotic solvents [60]. They may be also used to catalyze reactions between reagents contained in two different phases (either liquid/liquid or solid/liquid). The polyether is present only in "catalytic" amounts and the process is named "phase transfer catalyst" (TPC). Because of their "open" structure, crown ethers can extract cations from a crystalline solid. Depending on the catalyst used cations can be taken to a solid or liquid phase [61, 62]. According to Table 2, crown ethers display selectivity in complexation based on cavity and ion size.

Cation	Ionic Radius	Crown Ether	Cavity Diameter	Strongest Binding
Li ⁺	1.39Å	12-crown-4	1.2-1.4Å	Li ⁺
Na ⁺	1.94Å	15-crown-5	1.7-2.2Å	Na ⁺
K ⁺	2.66Å	18-crown-6	2.6-3.2Å	K ⁺

Table 2. The selectivity of crown ethers based on ion size.

Other related macropolycyclic ligands called "cryptates" (or cryptands or simply crypts) are more potent, selective and even stronger complexing agents for alkali metals. Besides, they show high complexing ability with alkaline earth cations, few transition and lanthanide ions also. The crypts are considered to be the three-dimensional equivalents of crown ethers but incorporate N as well as O atoms (sometimes S or P atoms also) to show higher denticity than the crown ethers. The molecules are appropriately cross-linked with donor atoms correctly positioned in the bridging group to encapsulate metal ions in cage-like structures. A typical crypt is the molecule $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$, called Crypt-222 (222 denotes the no. of ethereal O atoms in each N-N bridge) having the basic structure given in Fig. 11. Cryptates (meaning hidden) are so called because they wrap around and hide the cation. All these ligands form complexes with very high formation constants.



222 cryptand

Fig. 11. Structure of 222 cryptand.

The detection and elimination of heavy metal ions are important for life, environment and medicine sciences. Up to now, many analytical methods have been developed for detection of heavy metals [63, 64]. Very recently, smart responsive microcapsules capable of recognizing heavy metal ions based on crown ethers due to the "host-guest" complexation between the receptors and ions have been successfully developed by Pi et al [65]. Besides supramolecules like calixarenes and cyclodextrins, Schiff's bases (azomethines or imines) and crown ethers can be used as sensing material in the construction of potentiometric ion selective electrodes or catalytic applications [66-68]. Ganjali and co-workers studied different supramolecules based on Schiff's bases and crown ethers as potentiometric membrane sensors for cations and anions [69].

2.5 Cryptophanes

For the first time, cryptophanes were discovered by Collet and co-workers in 1981 [70]. Cryptophanes are molecular hosts having high binding affinities for small, neutral molecules, consisting of two cup-shaped, C_3 -symmetric, [1.1.1]orthocyclophane units, connected by three bridges (Y). These host-guest complexes are supramolecular assemblies mainly stabilized by van der Waals forces and specific π -interactions between the aromatic molecular cavity and the encapsulated guest. Most cryptophanes exhibit two diastereomeric forms (*syn* and *anti*), distinguished by their symmetry type. This general scheme offers a variety of choices (Y , R_1 , R_2 , and symmetry type) by which the shape, the volume, and the chemical properties of the generally hydrophobic pocket inside the cage can be modified, making cryptophanes suitable for encapsulating many types of small molecules and even chemical reactions. Fig. 12 represents the general structure of cryptophanes.

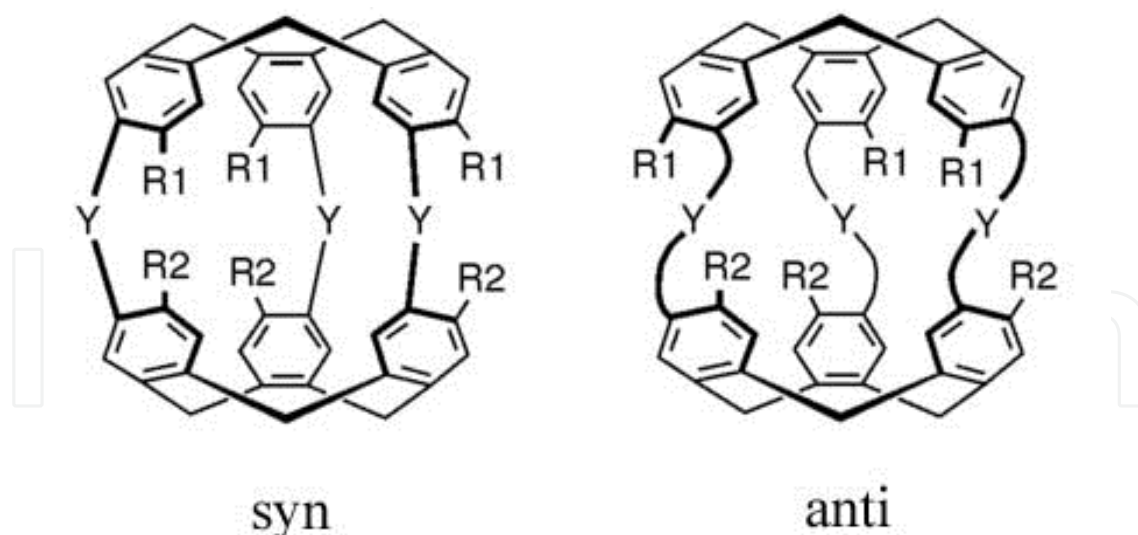


Fig. 12. General structure of cryptophanes.

Cryptophanes can be synthesized through any of three methods: (i) the “template method”, (ii) “two-step method”, or (iii) a “capping method”. “template method” was the first employed by Collet for the synthesis of cryptophanes [70]. A suitably substituted benzyl alcohol is first cyclized to form a trimeric cup. Additional benzyl alcohol substituents are then appended via a bridging Y group, and these groups are then subjected to an intramolecular cyclization to yield the corresponding cryptophanes. The initially formed C_3 -cup thus serves as a template for the second cup-forming reaction, with appreciable diastereoselectivity. This approach, for instance, allows the synthesis of cryptophanes that are asymmetric with respect to the peripheral substituents attached to the top and the bottom cups (R_1 and R_2 are different). Second, provided that the initially formed trimer can be resolved, this route can be employed to provide optically active *anti* cryptophanes of known absolute configuration. Method (ii), known as Collet’s “two step” synthesis, yields suitable cryptophanes in only two synthetic steps from readily available vanillyl alcohol ($R = OCH_3$, $X = OH$) [71]. In this approach, a monomer possessing two vanillyl alcohol residues is synthesized and then cyclized directly, under acidic conditions, to the corresponding cryptophanes. Notably, this reaction tends to display diastereoselectivity in favor of the chiral *anti* cryptophanes, making available some chiral *anti* cryptophanes that give low yields by the “template method”. Cram and co-workers demonstrated “capping method” (iii), the “capping” of one preformed C_3 -trimer with another, is also viable [72]. Though Cram’s synthesis involved the oxidative coupling of two identical cups possessing terminal acetylenic groups ($R = CH_3$; $X = OCH_2C CH$), “capping” one C_3 -trimer with a dissimilar trimer can also be envisaged (R_1 and R_2 , X_1 and X_2 are different). Though the yields of cryptophanes synthesized by the “capping” method were low ($< 15\%$), lessons learned from similar approaches toward the syntheses of (hemi)carcer and molecular containers suggest that it may be possible to improve yields by employing suitable guest templates. Depending on their structure, cryptophane cages are classified according to the following Table 3 [73].

Cryptophanes are interesting and versatile molecular receptors, whose complexation properties have been widely studied. For instance, cryptophanes are adapted for the recognition of dichloromethane [74, 75], xenon or biosensors based on xenon [76-79] and methane [80, 81].

Structure			Name	
Bridges Y	R ₁	R ₂	anti	syn
3 × O(CX ₂) ₂ O (where X is H or D)	OCX ₃	OCX ₃	A	
3 × O(CX ₂) ₂ O	OCH ₂ CO ₂ H	OCH ₂ CO ₂ H	A3	
3 × O(CX ₂) ₂ O	OCH ₃	H	C	D
3 × O(CH ₂) ₃ O	OCH ₃	OCH ₃	E	F
3 × O(CH ₂) ₃ O	OCH ₂ CO ₂ H	OCH ₂ CO ₂ H	E3	
3 × O(CH ₂) ₅ O	OCH ₃	OCH ₃	O	P
3 × O(CH ₂) ₅ O	OCH ₂ CO ₂ H	OCH ₂ CO ₂ H	O3	
3 × OCH ₂ C≡CC≡CH ₂ O	CH ₃	CH ₃	γ (gamma)	δ (delta)
2 × O(CH ₂) ₂ O, 1 × O(CH ₂) ₃ O	OCH ₃	OCH ₃	223	
2 × O(CH ₂) ₃ O, 1 × O(CH ₂) ₂ O	OCH ₃	OCH ₃	233	
2 × O(CH ₂) ₂ O, 1 × O(CH ₂) ₄ O	OCH ₃	OCH ₃	224	

Table 3. Classification of known cryptophane structures [73].

2.6 Porphyrins

Porphyryns are heterocyclic macrocycles composed of four modified pyrrole subunits interconnected at their *a* carbon atoms via methine bridges and they obey Hückel's rule for aromaticity, possessing $4n+2 = \pi$ electrons that are delocalized over the macrocycle. The synthetic chemistry of porphyryns is extremely rich, as its history began in the mid-1930s. The general synthetic route of porphyryns is shown in Fig. 13.

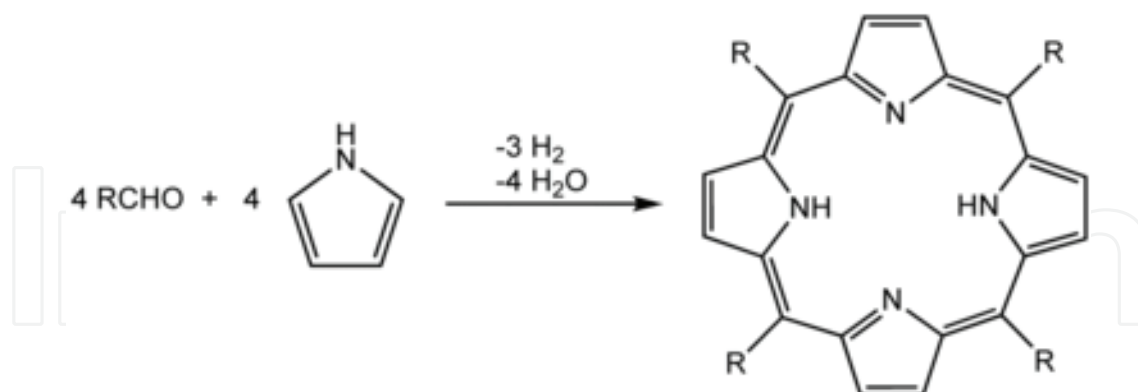


Fig. 13. General synthesize of porphyryns.

Porphyryns are also capable of being metallated and demetallated. Almost every metal in the periodic chart has been inserted into the porphyrin macrocycle but most typically are: Fe, Zn, Cu, and Ni, which can be inserted into the porphyrin cavity by using simple metal salts. Demetallation can usually be achieved by treatment with acids of various strengths. Porphyryns are often used to construct structures in supramolecular chemistry. These systems take advantage of the Lewis acidity of the metal, typically zinc. An example of a host-guest complex that was constructed from a macrocycle composed of four porphyryns

[82]. A guest-free base porphyrin is bound to the center by coordination with its four pyridine substituents. On the other hand, it is reported that multi-porphyrinic arrays attract more and more attention for the elaboration of photonic and electronic wires [83, 84]. In particular, metal ion coordination utilising ligation of the metallated porphyrin nucleus has proven efficient for positioning photoactive components. Because fullerenes are known as one type of acceptor with strong π -electron accepting ability, fullerene-porphyrin supramolecular assemblies have been studied extensively to generate photocurrents as well as to elucidate their unique photophysical and photochemical properties [85-89]. Supramolecular complexes were elaborated using these porphyrin-peptide oligomers as host and fullerenes as guest molecules, in collaboration with Professor Fukuzumi from Osaka University in Japan (Fig. 14). These supramolecular devices behave as organic photovoltaic cells and demonstrate remarkable enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and near-infrared regions with increasing the number of porphyrin units in a polypeptide structures. These results clearly show that the formation of molecular assembly between fullerene and multi-porphyrin arrays with a polypeptide backbone controls the electron-transfer efficiency in the supramolecular complex, which is essential for the light-energy conversion [90].

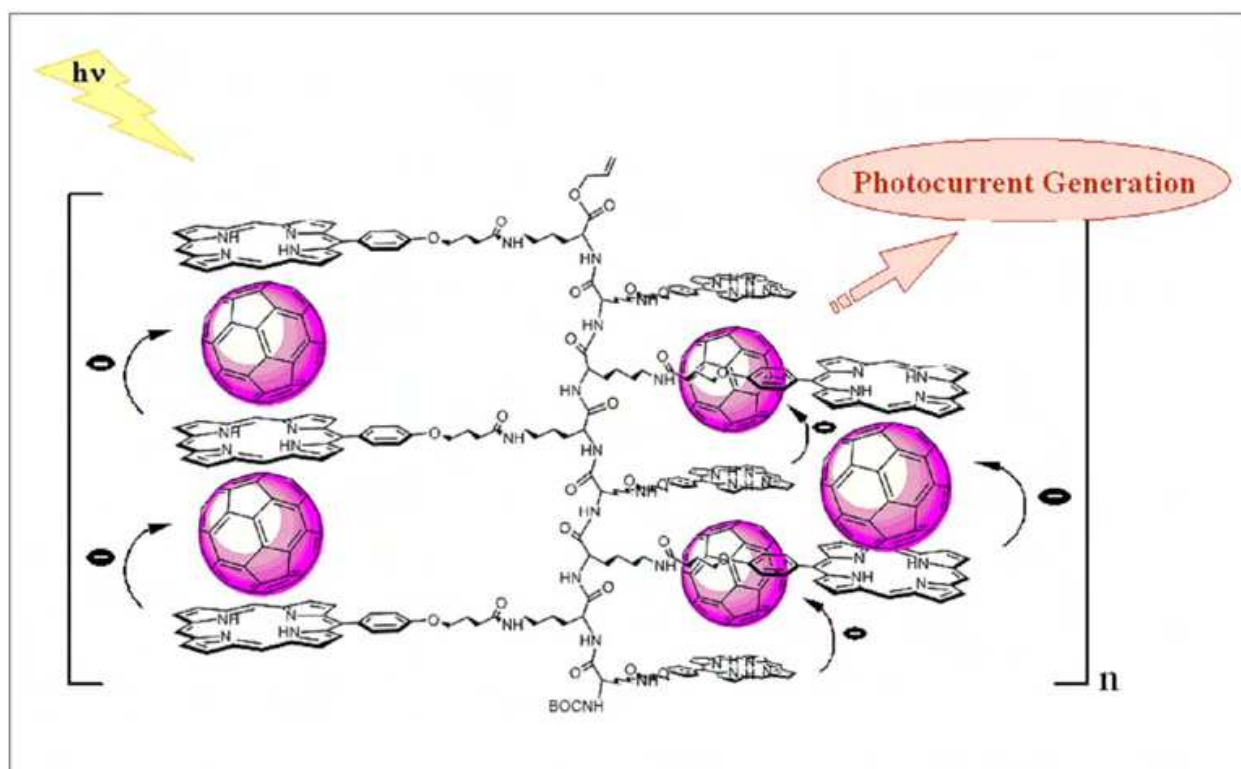


Fig. 14. A supramolecular consist of fullerene and multi-porphyrin arrays for the light-energy conversion [90].

Porphyrins with other guest molecules such as urea can provide a guideline to improve the structural homogeneity of the photonic wire [91]. It is possible that porphyrins are applied as guest molecules for special purposes. For example, a supramolecular system composed of photoswitchable β -cyclodextrin dimmers (host) and tetrakis-sulfonatophenyl porphyrin (guest) is a good candidate for using as photocontrollable (drug) delivery systems and might find application in, for example, photodynamic cancer therapy [92]. Besides, porphyrin

nanostructures are attractive building blocks because of their electronic, optical, and catalytic properties [93-95].

2.7 Cyclotrimeratrylenes

Cyclotrimeratrylene macrocycles are used in host-guest chemistry as molecular hosts. These compounds can be synthesised from veratrole alcohol by addition of a suitable acid which can be perchloric acid in methanol or formic acid or sulfuric acid in acetic acid [96].

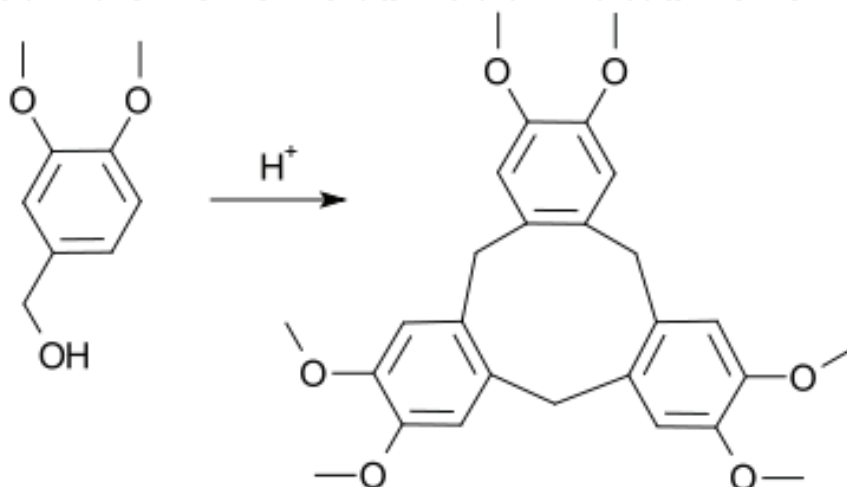


Fig. 15. General method for the preparation of cyclotrimeratrylene.

For the first time, Cyclotrimeratrylene (CTV) was synthesised by Gertrude Robinson in 1915 [97] and in 1965, Lindsey identified the correct structure [98]. The host molecule cyclotrimeratrylene (CTV) has a relatively rigid bowl shape, creating a molecular cavity, much like those seen in cone conformation calixarenes. The host-guest chemistry of CTV is, however, quite distinct from that of the calixarenes. CTV forms ball-and-socket type supermolecules with large neutral and cationic guest molecules such as fullerene- C_{60} [99] and $\{Na-[2.2.2]cryptate\}^+$ [100]. Fullerenes are able to generate efficiently cytotoxic singlet oxygen by energy transfer from the metastable fullerene triplet excited-state to molecular oxygen making them promising compounds for antitumor activities (photodynamic therapy). But, the low solubility of fullerenes in aqueous media limits their biological applications. To overcome this problem, several strategies have been developed such as the preparation of water soluble fullerene complexes with macrocyclic host systems [101, 102]. Therefore, Rio and Nierengarten synthesized water soluble supramolecular cyclotrimeratrylene- $[60]$ fullerene complexes for biological applications [103]. On the other hand, small organic solvent molecules have been encapsulated within the CTV molecular cavity [104, 105]. CTV has also proved to be a valuable building-block for the synthesis of more sophisticated host molecules such as cryptophanes and extended arm cavitands, where intracavity complexation of small and large guest molecules is common place. CTV has been employed as a host in coordination complexes or organometallic complex [106-108]. Recently, Nuriman and co-workers reported a novel chemosensor, based on tris[2-(4-phenyldiazenyl)phenylaminoethoxy]cyclotrimeratrylene (TPPECTV) for the colorimetric determination and visual detection of $Hg(II)$ ions. The preparation of TPPECTV and its structure are shown in Fig. 16 [109]. Schematic representation of heteroditopic hosts (CTVs) for ion-pair recognition is shown in Fig. 17 [110].

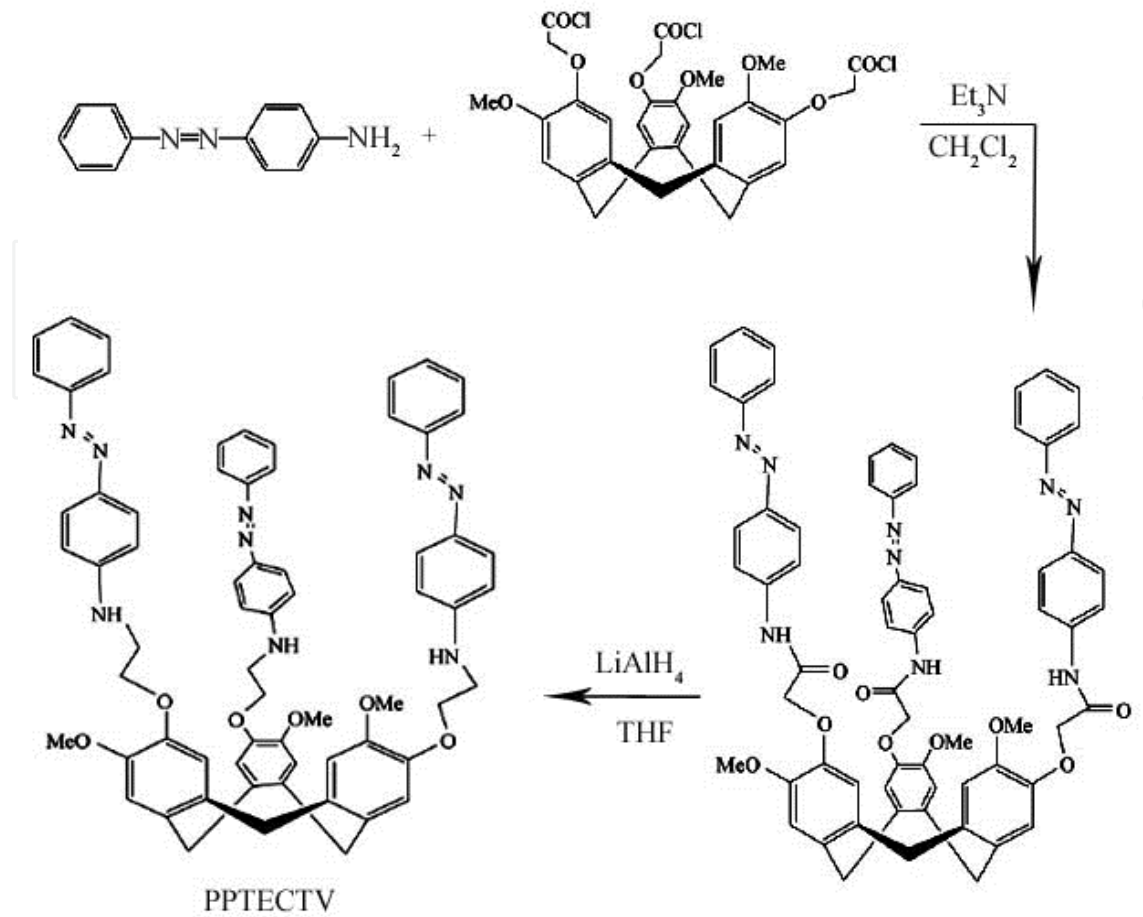


Fig. 16. The preparation of TPPECTV and its structure [109].

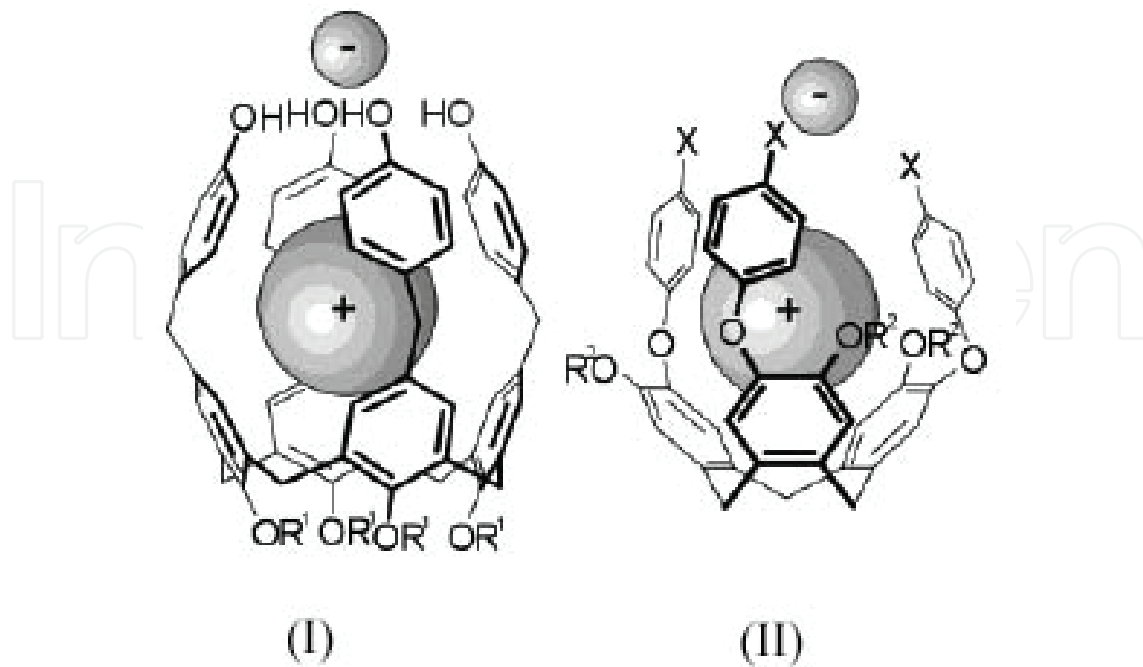


Fig. 17. Schematic representation of heteroditopic hosts (CTVs) for ion-pair recognition [110].

2.8 Carcerands

In 1983, Donald J. Cram introduced the concept of carcerand as a closed-surface binding host that can imprison simple organic molecules as guest [111], and in 1985, Cram and co-workers synthesized a typical carcerand by multiply binding cavitand (1) to (2) (Fig. 18) [112]. A carcerand as a synthetic host molecule completely entraps its guest so that it will not escape even at high temperatures. The generation of carcerands is based on calixarenes [113].

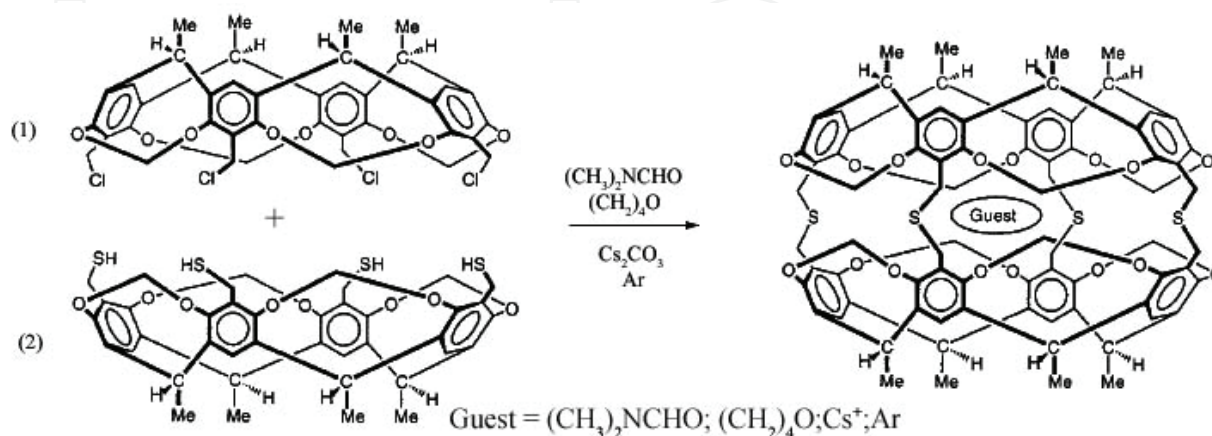


Fig. 18. Synthesized carcerand from (1) and (2) molecules [112].

The name carcerand is derived from the Latin word *carcer*, meaning "prison". In each carcerand, the incarcerated guests did not leave their prison, even at high temperatures. Complexes with permanently imprisoned guests are called "carceplexes" [114, 115]. In contrast, "hemicarcerands" incarcerate and liberate guests at elevated temperatures but form stable hemicarceplexes at ambient temperature [116]. It is reported that water-soluble hemicarcerands can be useful for drug delivery systems [117]. Piotrowiak and co-worker investigated novel water-soluble hemicarcerands to develop unique hybrid materials composed of semiconductor nanoparticles (TiO_2) and host-guest assemblies [118].

2.9 Zeolites

Zeolites as microporous aluminosilicate minerals are found in nature, and the zeolite mineral stilbite was first discovered in 1756 by the Swedish mineralogist A. F. Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Zeolites with microporous structure are known as a member of the family solids called "molecular sieves". The term "molecular sieve" refers to a particular property of these materials, the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential. Besides natural zeolites, synthetic zeolites can be obtained through hydrothermal or sol-gel method. Zeolite synthesis via a hydrothermal method occurs with reagents being a silica source, an alumina source, a mineralizing agent such as OH^- or F^- , and for higher Si/Al ratio zeolites, organic molecules as structure-directing agents. A schematic of the zeolite growth process is shown in Fig. 19 [119].

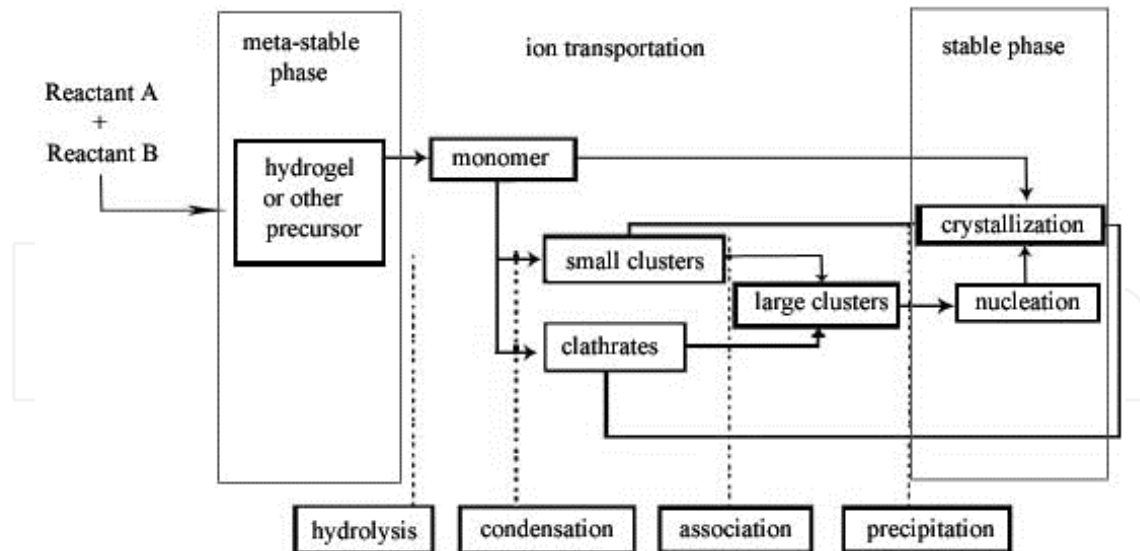


Fig. 19. Schematic representation of zeolite crystallization process [119].

Several independent processes are occurring in the medium, including nucleation of various structures, crystallization as well as dissolution of meta-stable phases. It is commonly observed that the conversion of the composition (gel or solution) to crystals is quite rapid once the crystallization process gets started. This suggests that nucleation is the rate-limiting step and is consistent with studies that report addition of seed crystals decrease the induction time [120]. Tezak suggested that rather than viewing the synthesis process as nucleation and crystallization, at least four subsystems be considered: (a) formation of simple and polymeric aluminosilicates, (b) aggregation of these complexes to form embryo, (c) nucleation as aggregate formation with a well ordered core and micelle formation (primary particles), and (d) aggregation of primary particles via oriented aggregation [121]. In sol-gel process, other elements (metals, metal oxides) can be easily incorporated but silicalite sol formed by the hydrothermal method is very stable.

2.9.1 Structure of zeolites

"Tectosilicates" (framework silicates) are inorganic 3D polymers based on SiO₄ tetrahedral units some of which can be replaced with AlO₄ tetrahedral units. Tectosilicates form 3/4 of the Earth's crust and zeolites are a sub-group of tectosilicates. Liebau and co-workers have proposed a classification for porous tectosilicates that is summarized in Fig. 20 [122].

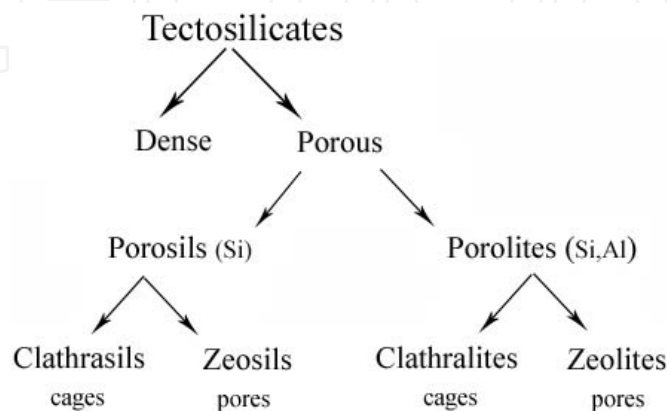


Fig. 20. Classification of porous tectosilicates [122].

Zeolites are composed of TO_4 tetrahedra ($T = \text{Si}, \text{Al}$) with O atoms connecting neighboring tetrahedra. For a completely siliceous structure, combination of TO_4 ($T = \text{Si}$) units in this fashion leads to silica (SiO_2), which is an uncharged solid. Upon incorporation of Al into the silica framework, the +3 charge on the Al makes the framework negatively charged, and requires the presence of extraframework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral. The zeolite composition can be best described as having three components:

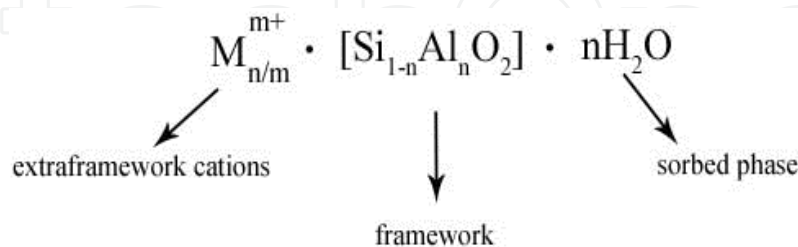


Fig. 21. Chemical composition of zeolites.

The extraframework cations are ion exchangeable and give rise to the rich ion-exchange chemistry of these materials. The novelty of zeolites stems from their microporosity and is a result of the topology of the framework. Other elements, such as B, Ge, Zn, P, and transition elements, can also be incorporated into the framework and are referred to as crystalline molecular sieves. Aluminophosphates (AlPOs) have strictly alternating AlO_2^- and PO_2^+ units, and the framework is neutral, organophilic and nonacidic. The alternation of Al or P leads to structures lacking in odd-numbered rings. Substitution of P by Si leads to silicoaluminophosphates (SAPOs), with cation-exchange abilities. Metal cations can also be introduced into the framework, including transition metal ions such as Co, Fe, Mn, and Zn. Discovery of these solids has led to the development of several new structures [123]. The framework composition depends on the synthesis conditions. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases.

Typically, in as-synthesized zeolites, water present during synthesis occupies the internal voids of the zeolite. The sorbed phase and organic non-framework cations can be removed by thermal treatment/oxidation, making the intracrystalline space available. The fact that zeolites retain their structural integrity upon loss of water makes them different from other porous hydrates, such as CaSO_4 . The crystalline nature of the framework ensures that the pore openings are uniform throughout the crystal and can readily discriminate against molecules with dimensional differences less than 1 \AA , giving rise to the name molecular sieves. According to the molar ratio of Si/Al, zeolites are classified to three types:

1. Low-silica or Al-rich zeolites
2. Intermediate silica zeolites
3. High-silica zeolites

About 40 natural zeolites are known. Most zeolites known to occur in nature are of lower Si/Al ratios, since organic structure-directing agents necessary for formation of siliceous zeolites are absent. Table 4 indicates the natural zeolites [124]. Sometimes natural zeolites are found as large single crystals, though it is very difficult to make large crystals in the laboratory. High-porosity zeolites such as faujasite (X,Y) are known as intermediate silica. Two natural zeolites that find extensive use are clinoptilolite (HEU) and mordenite (MOR) for ion-exchange (radioactive) agricultural uses and as sorbents. The catalytic activity of

natural zeolites is limited by their impurities and low surface areas. Another natural zeolite, erionite (ERI) has toxicity comparable to or even worse than some of the most potent forms of asbestos, especially in causing a form of lung mesothelioma.

Zeolites A and X (as low silica) were discovered by Milton and Breck at Union Carbide in 1959. These zeolites have the highest cation contents and are excellent ion-exchange agents. Breck reported the synthesis of zeolite Y in 1964, which spans a Si/Al ratio of 1.5–3.8 and with framework topology similar to that of zeolite X and the mineral faujasite. Decreasing the Al content led to both thermal and acid stabilities and paved the way for development of zeolite Y-based processes in hydrocarbon transformations. Large-pore mordenite, also with a Si/Al ratio of 5, was reported by Sand [125]. Zeolites with Si/Al ratios of 10–100 (or higher) such as ZSM-5 were reported by Mobil Research and Development Laboratories in the 1960s and 1970s [126]. Fig. 22 shows how the sodalite unit can be assembled to form common zeolitic frameworks. For example, in LTA, each sodalite(sod)-cage is connected to six nearest neighbouring sod-cages through double T4-rings (Fig. 22a) but in sodalite (SOD), each sod-cage is connected to six nearest neighbouring sod-cages through common T4-rings (Fig. 22b) [127].

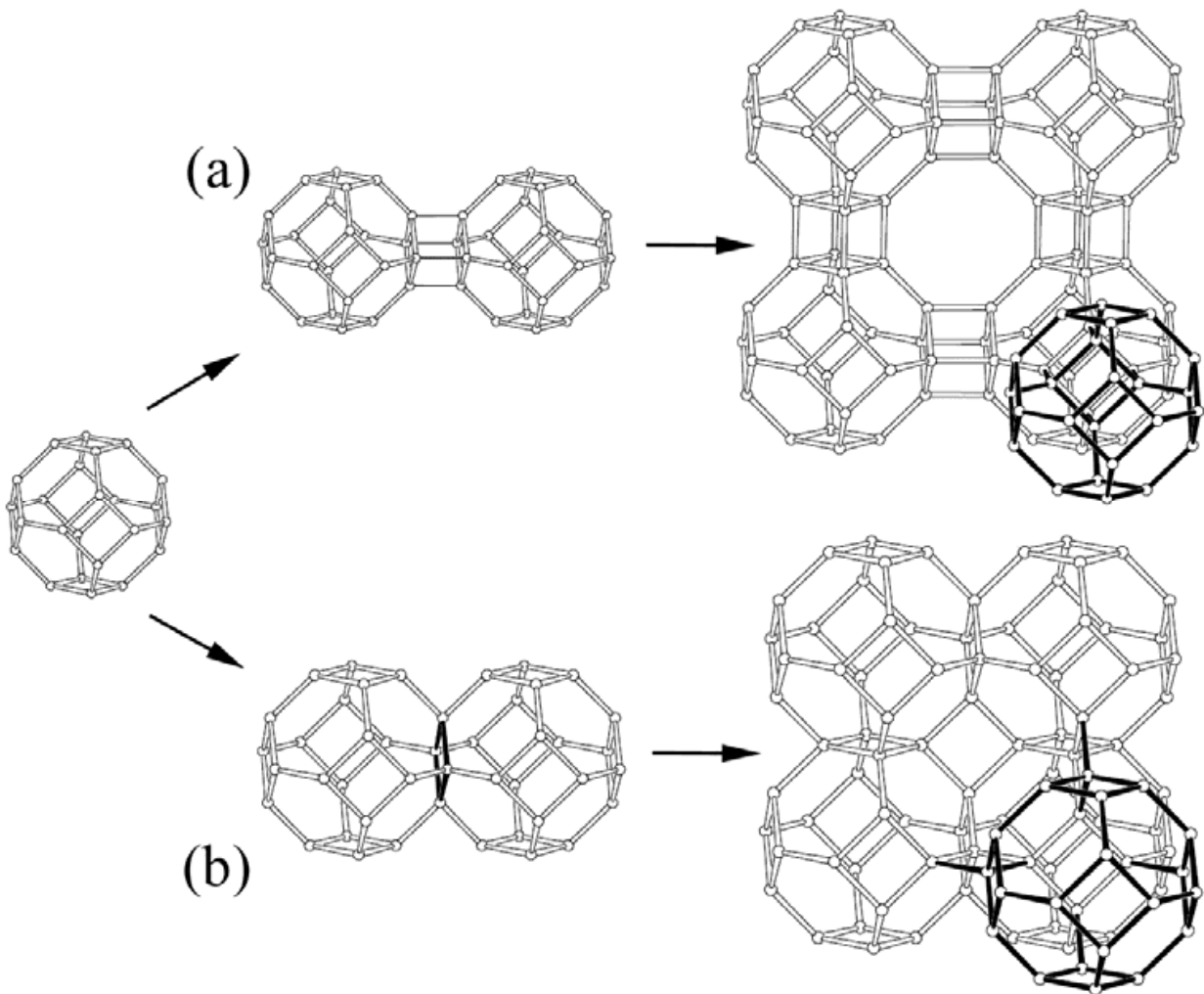


Fig. 22. Structure of LTA (a) and sodalite (b) [127].

Low silica $\text{Si/Al} \leq 2$	Intermediate silica $2 < \text{Si/Al} \leq 5$	High silica $5 < \text{Si/Al}$
ABW, Li-A(BW)	BHP, linde Q	ASV, ASU-7
AFG, afghanite ^a	BOG, boggsite ^a	BEA, zeolite β
ANA, analcime ^a	BRE, brewsterite ^a	CFI, CIT-5
BIK, bikitaite ^a	CAS, Cs-aluminosilicate	CON, CIT-1
CAN, cancrinite ^a	CHA, chabazite ^a	DDR, decadodelcasil 3R
EDI, edingtonite ^a	CHI, chiavennite ^b	DOH, dodecasil 1H
FAU, NaX	DAC, dachiardite ^a	DON, UTD-1F
FRA, franzinite	EAB, EAB	ESV, ERS-7
GIS, gismondine ^a	EMT, hexagonal faujasite	EUO, EU-1
GME, gmelinite ^a	EPI, epistilbite ^a	FER, ferrierite ^a
JBW, NaJ	ERI, erionite	GON, GUS-1
LAU, laumonite ^a	FAU, faujasite ^a , NaY	IFR, ITQ-4
LEV, levyne ^a	FER, ferrierite ^a	ISV, ITQ-7
LIO, liottite ^a	GOO, goosecreekite ^a	ITE, ITQ-3
LOS, losod	HEU, heulandite ^a	LEV, NU-3
LTA, linde Type A	KFI, ZK-5	MEL, ZSM-11
LTN, NaZ-21	LOV, lovdarite ^b	MEP, melanopholgite ^a
NAT, natrolite ^a	LTA, ZK-4	MFI, ZSM-5
PAR, partheite ^a	LTL, linde L	MFS, ZSM-57
PHI, phillipsite ^a	MAZ, mazzite ^a	MSO, MCM-61
ROG, roggianite ^a	MEI, ZSM-18	MTF, MCM-35
SOD, sodalite	MER, merlinoite ^a	MTN, dodecasil 3C
WEN, wenkite ^a	MON, montasommaite ^a	MTT, ZSM-23
THO, thomsonite ^a	MOR, mordenite ^a	MTW, ZSM-12
TSC, tschortnerite	OFF, offretite ^a	MWW, MCM-22
	PAU, paulingite ^a	NON, nonasil
	RHO, rho	NES, NU-87
	SOD, sodalite	RSN, RUB-17
	STI, stilbite ^a	RTE, RUB-3
	YUG, yugawaralite ^a	RTH, RUB-13
		RUT, RUB-10
		SFE, SSZ-48
		SFF, SSZ-44
		SGT, sigma-2
		SOD, sodalite
		STF, SSZ-35
		STT, SSZ-23
		TER, terranovaite
		TON, theta-1
		ZSM-48
		VET, VPI-8
		VNI, VPI-9
		VSV, VPI-7

^a Natural materials; ^b Beryllosilicates (natural).

Table 4. Classification of zeolites [124].

2.9.2 Zeolite properties

The decomposition temperature for Low-silica zeolites is ~ 700 °C, whereas completely siliceous zeolite, such as silicalite, is stable up to 1300 °C. Low-silica zeolites are unstable in acid, whereas high-silica zeolites are stable in boiling mineral acids, though unstable in basic solution. Cation concentration, siting, and exchange selectivity vary significantly with Si/Al ratios and play an important role in adsorption, catalysis, and ion-exchange applications. Though acid site concentration decreases with increase in Si/Al ratio, the acid strength and proton activity coefficients increase with decreasing aluminum content. The internal volume of zeolites consists of interconnected cages or channels, which can have dimensionalities of one to three. Pore sizes can vary from 0.2 to 0.8 nm, and pore volumes from 0.10 to 0.35 cm³/g. The framework can exhibit some flexibility with changes in temperature and via guest molecule-host interaction, as noted for the orthorhombic-monoclinic transformations in ZSM-5 [128].

2.9.3 Zeolite applications

Zeolites are widely used in primarily three applications, including:

1. Ion-exchange beds
2. Catalysts
3. Adsorbents

The major use of zeolites as ion-exchange agents is for water softening applications in the detergent industry and substitute use of phosphates. Natural zeolites find considerable use for removal of Cs⁺ and Sr²⁺ radioisotopes by ion exchange from radioactive waste streams [129]. Synthetic zeolites are extensively used as catalysts in the petrochemical industry. Zeolites confine molecules in small spaces, which cause changes in their structure and reactivity. The hydrogens formed of zeolites (prepared by ion-exchange) are powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation and cracking [130]. On the other hand, zeolites have the potential of purification and separation of gases, including the removal of H₂O, CO₂ and SO₂ from low-grade natural gas streams. Other separations include noble gases, N₂, O₂, freon and formaldehyde [131]. Besides, zeolites because of their microporous and nanoporous structure are used to form host-guest nanocomposite materials as host molecules for special applications, which discusses in future.

3. Host-guest chemistry

Commonly, there are four essential fields to study host-guest chemistry, including:

- Inclusion Compounds
- Intercalation Compounds
- Clathrates
- Molecular Tweezers

The definition of "inclusion compounds" is very broad, extending to channels formed between molecules in a crystal lattice in which guest molecules can fit. In host-guest chemistry, an inclusion compound is a complex in which one chemical compound (host) forms a cavity in which molecules of a second (guest) compound are located. In 1978, different cryptands with three-dimensional, two-dimensional, macrobicyclic, macrotricyclic and spheroidal topologies were introduced to form inclusion compounds [132]. Traditionally, inclusion compounds have been synthesized by crystallizing the host and guest compounds from a solution [133-135]. Whereas the choice of components available for the construction of such systems is limited by the solubilities of the host and the guest, the

limitations become more severe in multicomponent systems that require balancing the solubilities of several molecular species. A possible way to overcome solubility issues is through the use of mechanochemical methods. So that, Braga and co-workers have used the mechanochemical synthesis for the preparation of metal-organic intercalation compounds [136]. The design of synthetic strategies for creating novel host-guest inclusion compounds with zeolites provides the applications of these compounds in diverse areas of materials science, such as size /shape selective catalysis, nonlinear optics, quantum electronics, and photonics [137]. For example, cyclodextrins (CDs) with drugs can improve the solubility, stability, and bioavailability of drugs. The enhancement of drug activity and selective transfer or the reduction of side effects can also be achieved by inclusion compound formation [138]. Harris reported that thiourea inclusion compounds exhibit a wide range of interesting and important fundamental physicochemical properties [139].

In chemistry, "intercalation" is the reversible inclusion of a molecule (or group) between two other molecules (or groups). Many layered solids intercalate guest molecules. A famous example is the intercalation of potassium into graphite. Intercalation expands the "van der Waals gap" between sheets, which requires energy. Usually this energy is supplied by charge transfer between the guest and the host solid, i.e. redox.

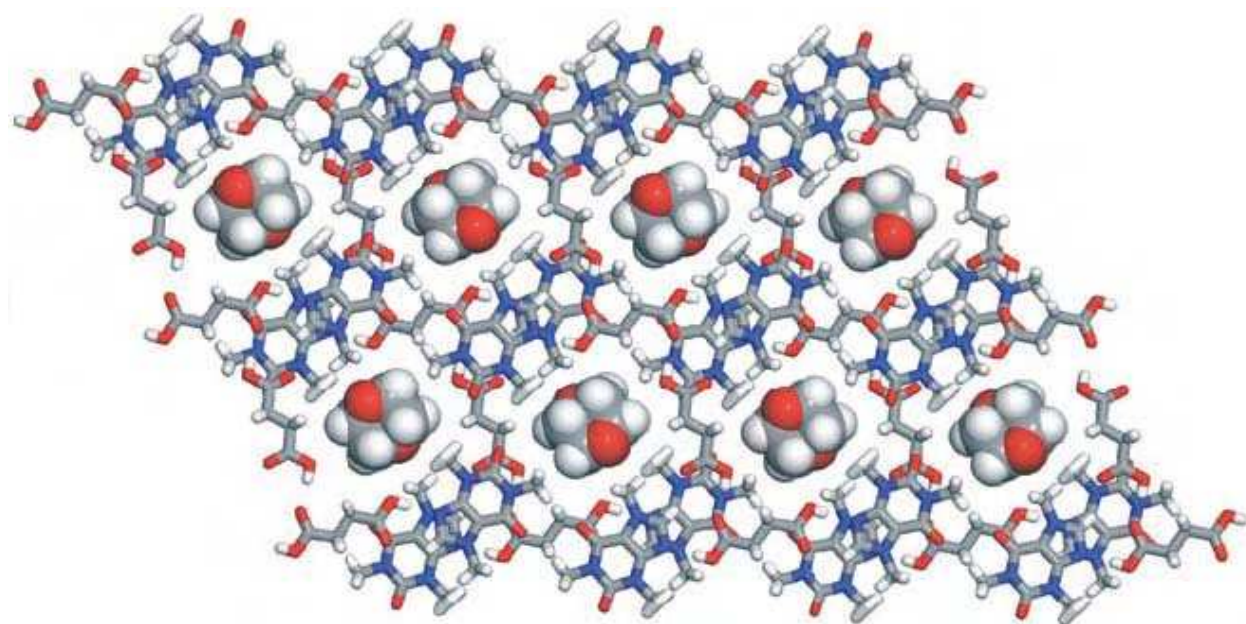


Fig. 23. An inclusion compounds consisting of a caffeine and succinic acid in a 1:1 stoichiometric ratio bound within 1,4-dioxane molecules reported by Jones [140]

Graphite intercalation compounds are formed by the insertion of atomic or molecular layers of a different chemical species called the intercalant between layers in a graphite host material, as shown in Fig. 24. The intercalation compounds occur in highly anisotropic layered structures where the intraplanar binding forces are large in comparison with the interplanar binding forces [141].

Aside from graphite, well known intercalation hosts are the layered dichalcogenides such as tantalum disulfide, molybdenum disulfide and iron oxychloride. Layered nanocomposites derived from two-dimensional MoS_2 host and coordination complexes exhibit good catalytic activities in the oxidization of sulfide ions into thiosulfate ions, due to their large surface areas [142]. It is reported that there are three ways to intercalate guest species in layered

inorganic hosts (inorganic-organic hybrid materials or nanocomposites): i) intercalation in layered host solids, ii) entrapping into inorganic matrices generated by sol-gel, and iii) grafting of macrocycles on inorganic surfaces. So that, the resulting nanocomposites have useful applications as solid electrolytes, ion-selective membranes and electrochemical sensors [143].

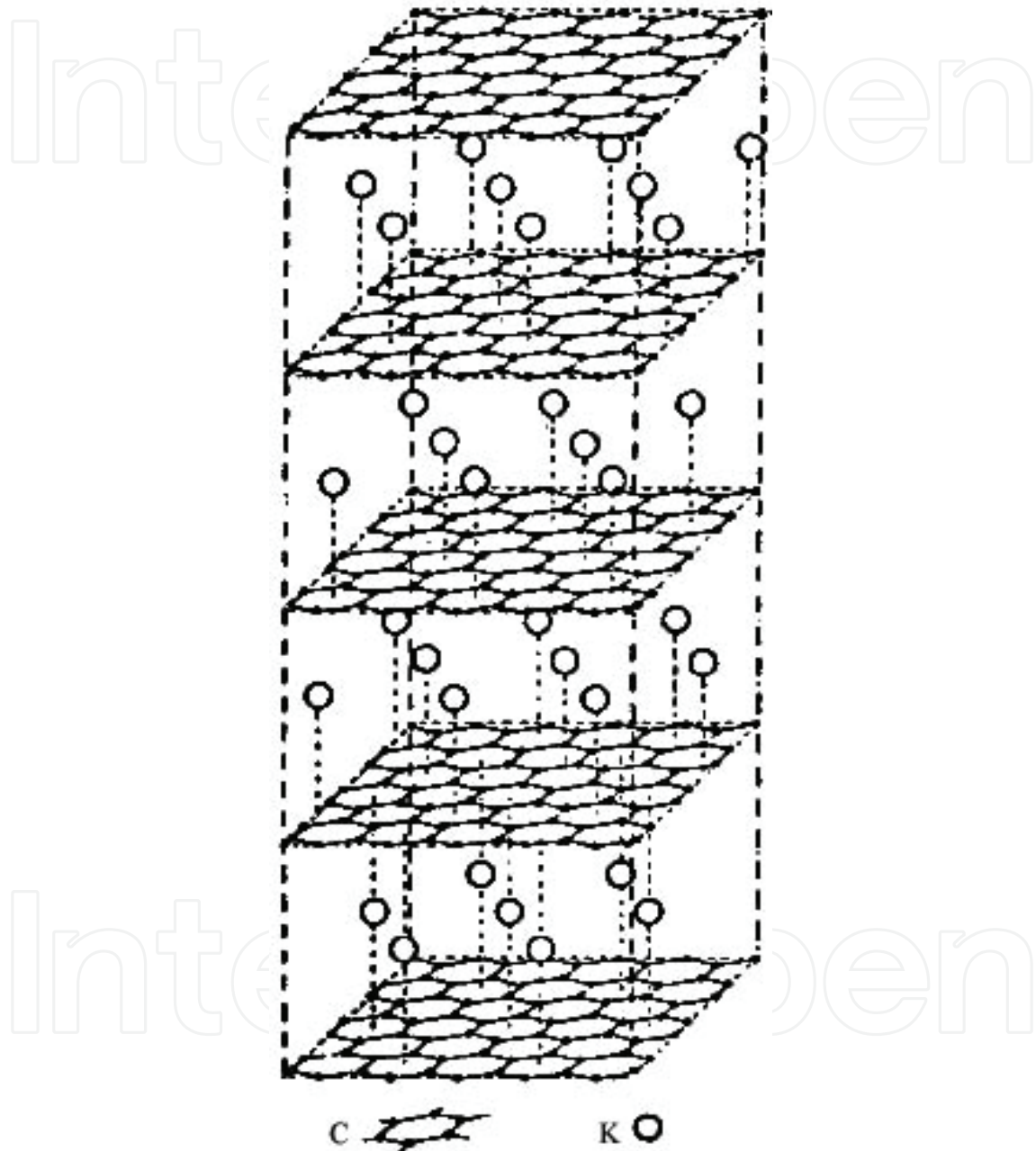


Fig. 23. The intercalation of potassium (guest) into graphite layers (host) [141].

"Clathrate compounds" or cage compounds are consisting of a lattice of one type of molecule trapping and containing a second type of molecule. In 1810, a clathrate hydrate discovered by Humphry Davy is a special type of gas hydrate in which a lattice of water molecules encloses molecules of a trapped gas. Very recently, Lee et al. studied ionic clathrate hydrates [144]. Clathrate hydrates are inclusion compounds where the host is a

polyhedral framework built of hydrogen-bonded water molecules in which guest molecules are trapped. Host-guest interactions are usually van der Waals in nature. Structures of clathrate hydrates are classified by the type of water framework, which is considered to be a three-dimensional packing of polyhedral cages with tetra-, penta-, and hexagonal faces, oxygen atoms as vertices, and hydrogen bonds as edges. The cages can act as hosts to a variety of guest molecules, from inert gases to large organic molecules (including those with hydrophilic groups). The shape and size of the guest molecules define the structural type of hydrate formed.

According to available investigations, ionic clathrate hydrates involve acid and base clathrate hydrates. In some strong acids, anion guests are enclathrated into the protonated host lattice to form ionic clathrate hydrates such as HPF_6 hydrate with a cubic $Im3m$ structure [145, 146] but, some types of ionic clathrate hydrates are composed to cationic guests and a host lattice balanced by anions such as OH^- , F^- and Br^- , showing strong or weak basicity in many cases [147-149].

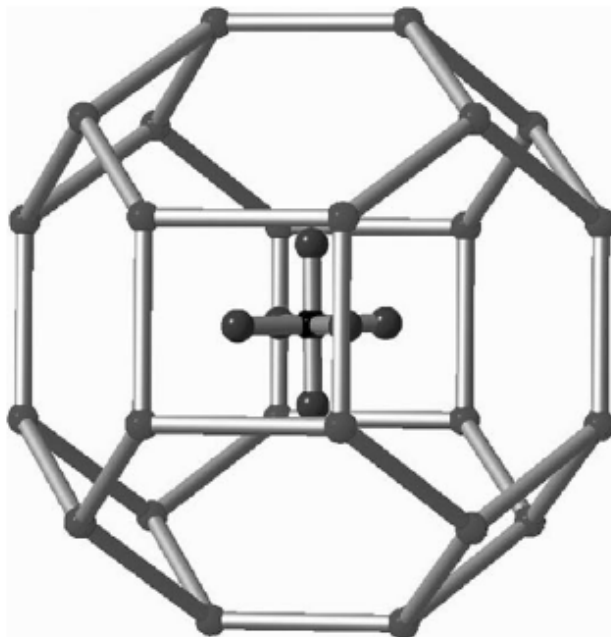


Fig. 24. The truncated-octahedral cage of HPF_6^- hydrate and PF_6^- is encaged into the water cage [145].

A number of hydrates of quaternary ammonium salts (QAS) can form ionic clathrate hydrates. The most usual types of QAS hydrates are the tetra-nbutyl ammonium ($(\text{nBu})_4\text{N}^+$) and tetra-iso-amyl ammonium ($(\text{i-amyl})_4\text{N}^+$) hydrates. So that, these types of ionic clathrate hydrates are also called “semi-clathrate” because some cages are partially broken in order to encage the large cations [150]. Recently, ionic clathrate hydrates have received increased attention arising from their potential applications in various fields, including solid electrolytes, gas separation, and gas storage [151-153]. Kamata et al. [154, 155] examined the ability of the $(\text{nBu})_4\text{NBr}$ clathrate hydrate to separate the gas mixtures. Small gas molecules such as CH_4 , N_2 and H_2S were selectively encaged in the cages of this hydrate during clathrate formation, whereas larger gas molecules such as C_2H_6 and C_3H_8 were not incorporated into the $(\text{nBu})_4\text{NBr}$ double clathrate hydrates. Among the various gas molecules, H_2S was found to be the most efficient guest for the $(\text{nBu})_4\text{NBr}$ double clathrate hydrate owing to its molecular size and solubility in water.

Among the various types of artificial receptors molecular "tweezers" has attracted more and more attention in molecular recognition, mimic enzyme catalysis, the resolution of racemates as well as molecular devices [156-159]. Related studies by Whitlock [160, 161] and Zimmerman and their co-workers [162-164] enabled the development of a subset of this receptor class that is referred to as "molecular tweezers". The open cavity of the molecular tweezers may bind guests using non-covalent bonding which includes hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π - π interactions, and/or electrostatic effects. These complexes are a subset of macrocyclic molecular receptors and their structure is that the two "arms" that bind the guest molecule between them are only connected at one end. The reduction of high cholesterol levels in humans which result from the consumption of dairy products is very essential for human health. Several studies have focused on receptors for cholesterol in order to extract the sterol from the food source [165]. Molecular tweezer type receptors have been developed for this purpose [166-168].

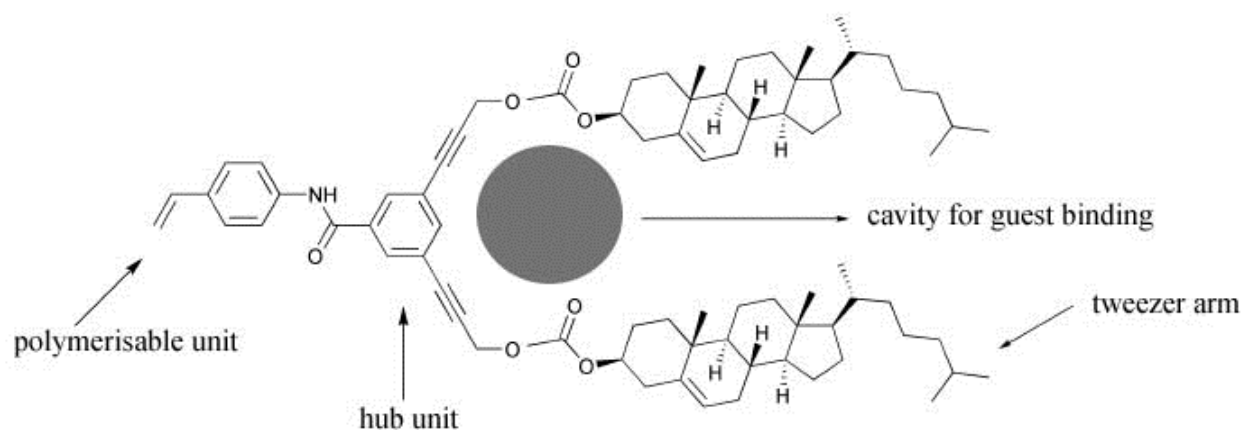


Fig. 25. Molecular tweezer type receptor for cholesterol [168].

4. Zeolite encapsulation and host-guest nanocomposite materials

A "nanocomposite" consists of multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material [169]. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the conventional composite materials due to the exceptionally high surface to volume ratio. Some zeolites (pore size from 0.2 to 0.8 nm) because of their nanoporous structure are used to form host-guest nanocomposite materials as host molecules for special applications. Recently, encapsulation of different guest molecules into zeolites has attracted much interest due to the possibility of obtaining stable structures with potential applications in different fields [170-178]. Herein, several zeolite encapsulation systems and their applications are studied.

4.1 Host (zeolite)/guest (transition metal complex) nanocomposites: catalytic applications

Zeolites and zeotypes (molecular sieves), owing to their varied intrinsic properties (e.g., acidity, basicity, redox behavior, etc.), channel sizes, high surface areas, thermal and chemical stabilities and channel structures (shape selectivity) have been extensively used to form heterogeneous catalysts with transition metal complexes. The encapsulation of

transition metal complexes within small voids in zeolites or other microporous solids can be used to contain and protect active structures and to select reactants, products, or transition states, thus providing diverse strategies for the design and synthesis of more effective catalysts. The small and uniform size of channels and voids within crystalline microporous solids allows selective access of molecules to intracrystalline active sites based on size or shape.

Although homogeneous metal complex catalysts exhibit good activities and selectivities, heterogenization of homogeneous metal complex catalysts by encapsulating them inside zeolites offers the advantages of both homogeneous and heterogeneous counterparts such as: (1) easy separation of the catalysts from the reagents and reaction products; (2) simplification of methods to recycle expensive catalysts; (3) nonvolatile and nontoxic characteristics to high molecular weight zeolite backbones; (4) minimization of certain catalyst deactivation pathways by site isolation [179]. There are three approaches to synthesize zeolite encapsulated metal complexes, including:

1. Zeolite Synthesis Method (ZS)
2. Flexible Ligand Method (FL)
3. "Ship-in-a-Bottle"

In zeolite synthesis method (ZS), transition metal complexes, which are stable under the condition of zeolite synthesis such as high pH and high temperature, are added to the synthesis mixture. The resulting zeolite encapsulates the metal complexes in its cavity. In flexible ligand method (FL), if the size of ligand is smaller than the diameter of zeolite channels, the ligand is diffused freely through the zeolite channels. The ligand reacts easily with the desired metal ions which have been previously exchanged in the supercages of zeolite and makes a stable metal complex. When the ligand size is larger than the diameter of zeolite channels, then template synthesis (TS) method is used. In this method, the molecules of the ligand species are diffused freely into the zeolite cavity where they assemble around the resident metal ions (fixed by ion exchange) in the zeolite cavity. The size of the synthesized metal complex will be too large to escape out from the supercages of zeolite. These encapsulated metal complexes in the cavity of zeolite have been called by several research groups as "ship-in-a-bottle" [180, 181].

4.1.1 Cyclohexane oxidation reactions

To produce more valuable organic compounds such as alcohols, aldehydes, and ketones, the oxyfunctionalization of inexpensive hydrocarbons requires the selective oxidation of strong C-H bonds. Because alcohols and ketones are known as important intermediate materials for the manufacture of many important products such as: fiber, drugs and fragrance. Amongst heterogeneous catalysts, zeolite encapsulated transition metal complexes catalysed oxidation of cyclohexane into a variety of products such as cyclohexanol and cyclohexanone has received much attention [182-184]. Maurya and co-workers introduced a new catalyst based on oxovanadium(IV) and copper(II) exchanged zeolite-Y for the oxidation of styrene, cyclohexene and cyclohexane [182]. As shown in Table 5, oxidation of cyclohexane catalysed by [Cu(sal-dach)]-Y and [VO(sal-dach)]-Y gave cyclohexanone, cyclohexanol and cyclohexane-1,2-diol with different conversion and selectivity in the presence of H₂O₂. Amongst the various products formed, the selectivity of cyclohexanol was found to be highest (91.2 % for [Cu(sal-dach)]-Y and 82.2 % for [VO(sal-dach)]-Y) while selectivities of other two products were much less. On the other hand, catalytic potential of neat complexes has been compared. These results revealed that a maximum of 78.1% conversion of

cyclohexane catalysed by [VO(sal-dach)]-Y and only 21.0% conversion by [Cu(sal-dach)]-Y with major reaction products of cyclohexanone, cyclohexanol and cyclohexane-1,2-diol have been obtained. The structure of [VO(sal-dach)] and [Cu(sal-dach)] complexes are shown in Fig. 26.

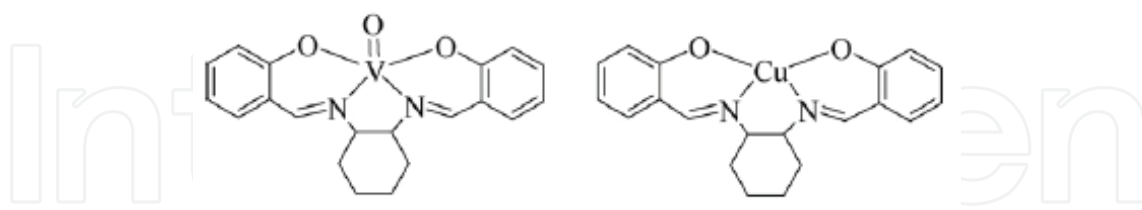


Fig. 26. The structure of [VO(sal-dach)] and [Cu(sal-dach)] complexes [182].

Catalyst	Conversion (%)	Selectivity (%)	
		Cyclohexanol	Cyclohexanone
[VO(sal-dach)]-Y	78.1	82.2	4.8
[Cu(sal-dach)]-Y	21.0	91.2	2.0
[VO(sal-dach)]	36.8	93.1	2.4
[Cu(sal-dach)]	40.9	90.3	1.8

Table 5. Effect of different catalysts on the oxidation of cyclohexene and product selectivity [182].

Besides zeolite encapsulated transition metal complexes, metal complexes with Schiff-base ligands can be entrapped in the nanocavity of zeolite-Y. Recently, two novel host (zeolite-Y)/ guest (Schiff base metal complex) nanocomposites were synthesized for the oxidation of cyclohexane by our group [183, 184]. Metal complexes of Mn(II), Co(II), Cu(II) and Ni(II) with tetradentate Schiff-base ligand, (salicylaldehyde)oxaloyldihydrazone, were entrapped in the nanocavity of zeolite-Y via a "ship-in-a-bottle" approach (Fig. 27).

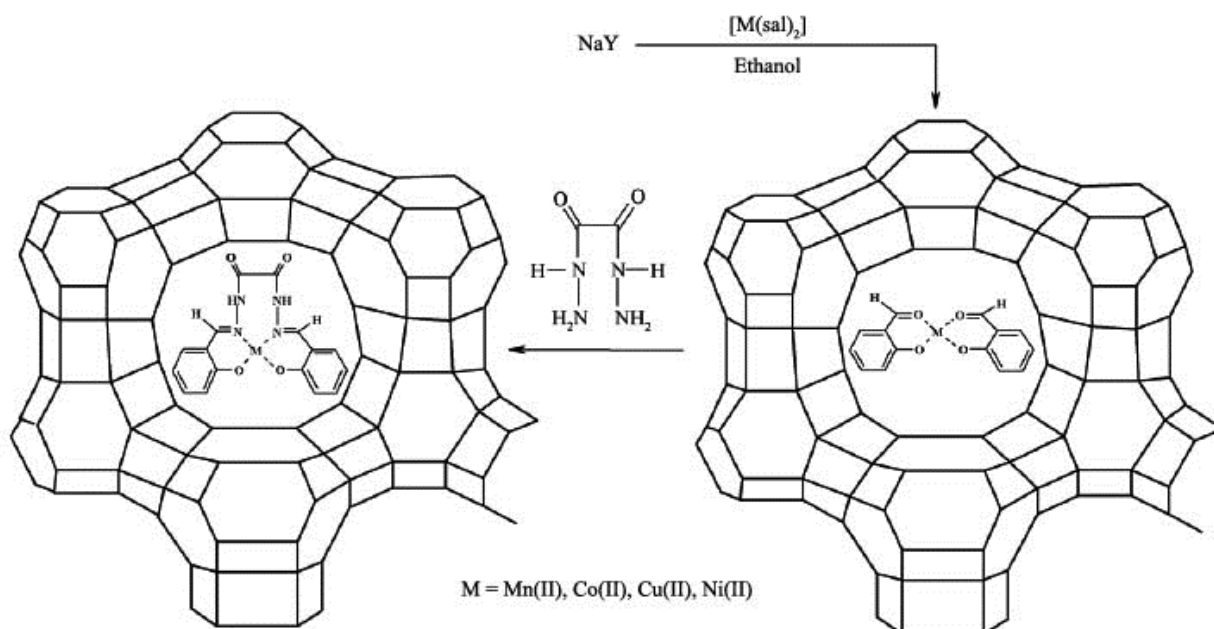


Fig. 27. Schiff-base ligand entrapped in the nanocavity of zeolite-Y [183].

The catalytic effects of Schiff base metal complexes encapsulated in zeolite-Y and neat complexes were studied on the oxidation of cyclohexane in the presence of hydrogen peroxide in CH₃CN and the results are shown in Table 6 [183]. Fig. 29 and Fig. 30 show the catalytic effects of octahydro-Schiff base metal complexes and octahydro-Schiff base metal complexes encapsulated in zeolite-Y, respectively.

Catalyst	Conversion (%)	Selectivity (%)	
		Cyclohexanol	Cyclohexanone
[MnL]	12.6	35.9	64.1
[CoL]	31.2	31.6	68.4
[NiL]	5.7	29.5	70.5
[CuL]	46.8	28.4	71.6
[MnL]-NaY	8.4	25.9	74.1
[CoL]-NaY	28.6	22.4	77.6
[NiL]-NaY	2.1	20.3	79.7
[CuL]-NaY	42.9	17.5	82.5
Cu(II)-NaY	10.6	11.7	88.3

Table 6. Oxidation of cyclohexane with H₂O₂ catalyzed by host-guest nanocomposites and neat complexes [183].

According to Table 6, it is found that cyclohexanone is selectively formed in the presence of all catalysts and the catalytic potential of Schiff base metal complexes encapsulated in zeolite-Y decreases in the series [CuL]-NaY > [CoL]-NaY > [MnL]-NaY > [NiL]-NaY.

For the first time, transition metal (M = Mn(II), Co(II), Ni(II) and Cu(II)) complexes with octahydro-Schiff base (H₄-N₄O₄) have been encapsulated in nanopores of zeolite-Y; [M([H]₈-N₄O₄)]@NaY; through Flexible Ligand Method (FLM) and utilized as oxidation catalysts [184]. The formation of these host-guest nanocomposite materials was illustrated in Fig. 28.

The results clearly suggest that [Cu₂([H]₈-N₄O₄)]@NaY efficiently catalyses the conversion of cyclohexane to cyclohexanol and cyclohexanone with 59.3% and 40.7% selectivity, respectively.

4.1.2 Cyclohexene oxidation reactions

The encapsulated complexes catalyse the cyclohexene oxidation reactions in good yield. Under the optimized conditions, the oxidation of cyclohexene gave cyclohexeneoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as major products (Fig. 31). Various high reactive zeolite encapsulated complex catalysts used for the oxidation of cyclohexene were illustrated in Table 7.

Besides the type of catalyst, temperature and amount of catalyst effect on the catalytic activity and product selectivity [193-195]. Nanoscale microreactor containing (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene)nickel(II) were entrapped in the supercage of zeolite Y and cyclohexene was catalytically oxidized in the presence of molecular oxygen and [Ni(Me₆[14]aneN₄)]²⁺-NaY. Effects of temperature and amount of catalyst on the reactivity and product selectivity were investigated. These results were illustrated in Table 8 and Table 9 [194].

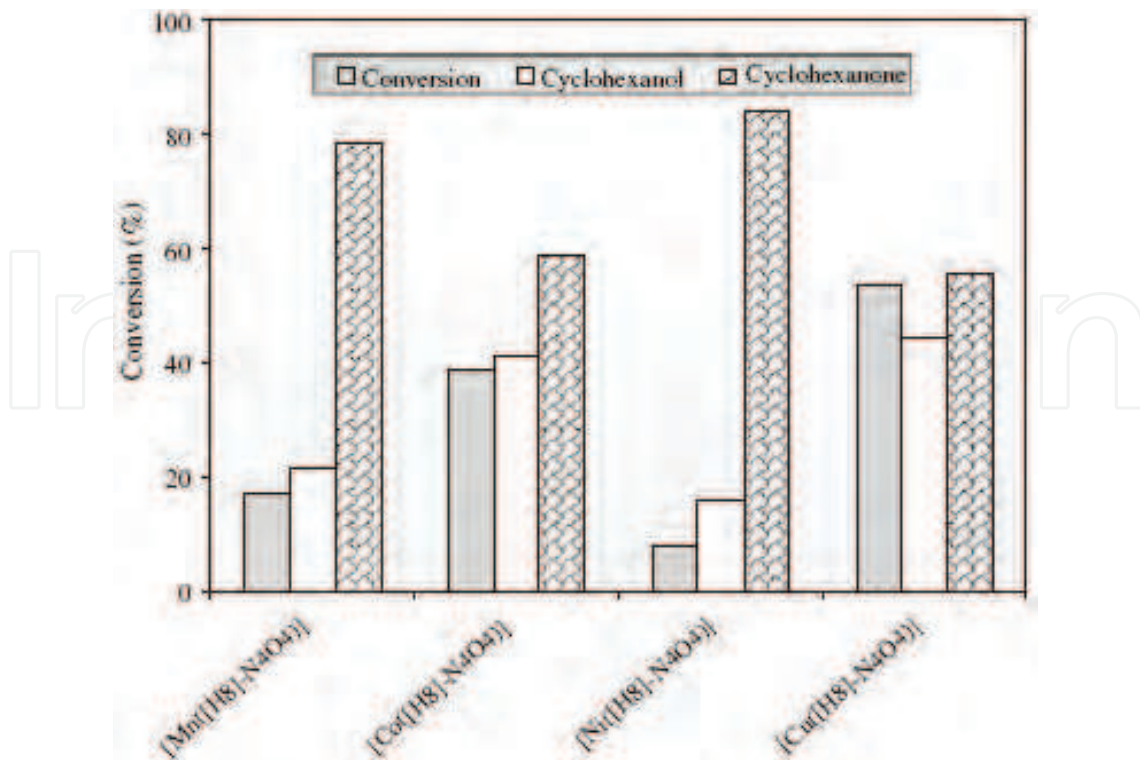


Fig. 29. Conversion and oxidation products distribution in CH_3CN with neat octahydro-Schiff base complexes in the oxidation of cyclohexane with H_2O_2 [184].

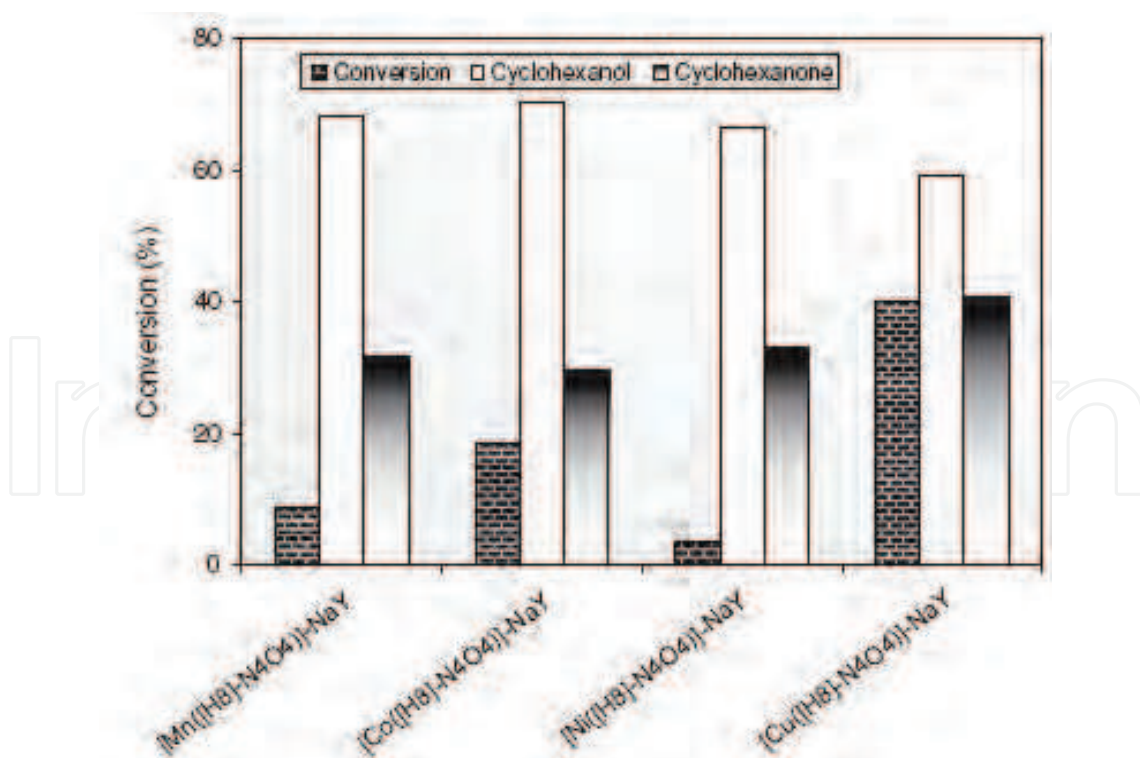


Fig. 30. Conversion and oxidation products distribution in CH_3CN with octahydro-Schiff base ($\text{H}_4\text{-N}_4\text{O}_4$) encapsulated in nanopores of zeolite-Y in the oxidation of cyclohexane with H_2O_2 [184].

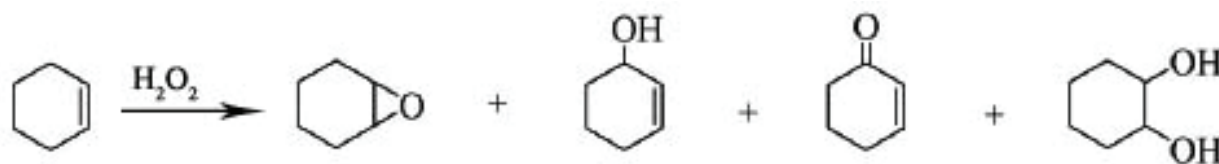


Fig. 31. Oxidation of cyclohexene.

Catalyst	Conversion (%)	Major Product	Ref.
[VO(sal-dach)]-Y	86.6	2-cyclohexene-1-one	182
[Ni(Bzo ₂ [14]aneN ₄)] ⁺² -NaY	49.6	2-cyclohexene-1-ol	185
[Mn(H ₄ C ₆ N ₆ S ₂)]-NaY	90.3	2-cyclohexene-1-one	186
[Mn(Bzo ₂)[12]aneN ₄] ⁺² -NaY	80.34	di-2-cyclohexenylether	187
[Ni((Benzyl) ₂ [16]aneN ₆)] ⁺² -NaY	59.7	2-cyclohexene-1-ol	188
[Ni((Benzyl) ₂ Bzo ₂ [14]aneN ₆)] ⁺² -NaY	68.7	2-cyclohexene-1-ol	189
[Mn(sal-2,6-py)]-NaY	92.5	2-cyclohexene-1-one	190
[Ni((C ₆ H ₅) ₂ [12]1,3-dieneN ₂ O ₂)] ⁺² -NaY	67.5	2-cyclohexene-1-ol	191
[Ni([H] ₂ -N ₄)] ⁺² -NaY	70.8	2-cyclohexene-1-ol	192

Table 7. High reactive zeolite encapsulated complex catalysts used for the oxidation of cyclohexene.

Temperature (°C)	Conversion (%)	Selectivity (%)	
		2-Cyclohexene-1-ol	2-Cyclohexene-1-one
50	4.8	60.2	39.8
60	10.6	62.6	37.4
70	61.6	65.5	34.5
80	20.6	68.6	31.4

Table 8. Effect of temperature on the reactivity and product selectivity [194].

Amount of catalyst (mg)	Conversion (%)	Selectivity (%)	
		2-Cyclohexene-1-ol	2-Cyclohexene-1-one
5	53.2	53.6	46.4
6	54.5	55.4	44.6
7	56.3	57.6	42.4
8	57.4	59.4	40.6
9	59.6	61.3	38.7
10	61.6	65.5	34.5
11	59.1	60.6	39.4
12	58.3	51.4	48.6

Table 9. Effect of amount of catalyst on the reactivity and product selectivity [194].

It is found that the reactivity and selectivity to 2-cyclohexen-1-ol increase in the range of 50–70 °C. On the other hand, the optimized amount of catalyst is 10 mg with the highest conversion and selectivity to 2-cyclohexen-1-ol.

4.1.3 Phenol and alcohol oxidation reactions

Host (zeolite)/guest(metal complex) nanocomposite materials (HGNMs) can be used as suitable catalysts for oxidation of aromatic and aliphatic alcohols. Catalytic activity of [Cu(salpn)]-Y in the oxidation of phenol to a mixture of catechol and hydroquinone using H₂O₂ as an oxidant has been studied by Maurya and co-workers and the best suited reaction conditions have been optimized by considering the effect of solvents used, concentration of substrate, temperature, reaction time, amount of catalyst and oxidant [196]. Under the best suited conditions, the selectivity towards the formation of catechol and hydroquinone is about 80 and 20%, respectively. Very recently, solvent free catalyzed oxidation of benzyl alcohol by 7, 16-diacetyl[Cu(Me₄(Bzo)₂[14]tetraeneN₄)]-NaY was reported [197]. Saha et al. showed that the complex Cu(salen) [salen = N,N0-(ethylene)bis(salicylaldiimine)] encapsulated in NaY zeolite exhibits remarkable catalytic activity for oxidizing of 1-naphthol and norbornene [198]. Herein, we summarize several effective HGNM catalysts for the oxidation of phenol, benzyl alcohol and cyclohexanol (Table 10).

Functionalization of carbon nanotubes with Schiff base complexes is an effective way to enhance their physical and chemical properties, and improve solubility. Our experimental results showed that functionalized multi-wall carbon nanotubes (MWNTs) by Schiff-base complexes can catalyze the oxidation of aliphatic and aromatic alcohols into the corresponding carboxylic acids and ketones in the presence of H₂O₂ in good yields [206, 207].

4.1.4 Other catalytic applications

Besides above mentioned catalytic application of HGNMs, these novel materials can catalyze other important reactions in good yield such as: hydroxylation [208-214], oxidation of sulfides and ethers [215-219] and epoxidation [220-222].

Catalyst	Substrate	Conversion (%)	Major Product	Ref.
[Cu((C ₆ H ₅) ₂ [13]1,4dieneN ₄ O ₂)] ⁺² -NaY	Cyclohexanol	88.6	Cyclohexanone	199
[Cu((Benzyl) ₂ Bzo ₂ [14]aneN ₆)] ⁺² -NaY	Benzyl alcohol	75.7	Benzaldehyde	200
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)] ⁺² -NaY	Benzyl alcohol	83.1	Benzaldehyde	201
[Cu(Me ₄ [14]aneN ₈)] ⁺² -NaY	Benzyl alcohol	73.2	Benzaldehyde	202
[VO ₂ (sal-ambmz)]Y	Phenol	43.9	Catechol	203
[Cu(Eto-salen)-NaY	Phenol	44	Catechol	204
[Ni(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)] ⁺² -NaY	Phenol	60.3	Catechol	205

Table 10. Several effective HGNM catalysts for the oxidation of phenol and alcohols.

5. Conclusions

A topic of great interest in recent years is the synthesis of molecules (hosts) capable of encapsulating smaller molecules (guests) within open interior cavities containing portals allowing the smaller guest species to enter and depart. Such molecules can serve as models of molecular recognition in biological systems and have provided better understanding of the nature of hydrophobic and van der Waals interactions in aqueous solutions. Besides catalytic applications of host-guest nanocomposite materials, these materials because of

their nano-size dimension can be used as gas adsorption and separation [223-225] sunscreen additives for reducing adverse effects from UV [226] and for water splitting [227].

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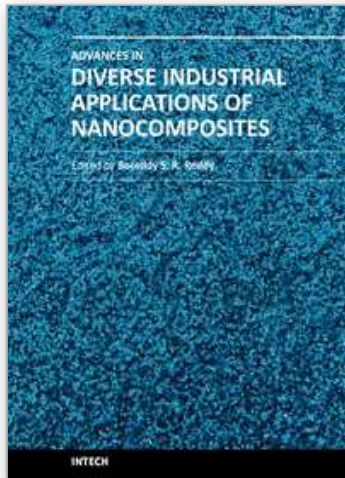
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Nanocomposites are attractive to researchers both from practical and theoretical point of view because of combination of special properties. Many efforts have been made in the last two decades using novel nanotechnology and nanoscience knowledge in order to get nanomaterials with determined functionality. This book focuses on polymer nanocomposites and their possible divergent applications. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications can already be found in industry. This book comprehensively deals with the divergent applications of nanocomposites comprising of 22 chapters.

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