Synthesis of nanoparticles templated by zeolite matrices: Advantages and disadvantages

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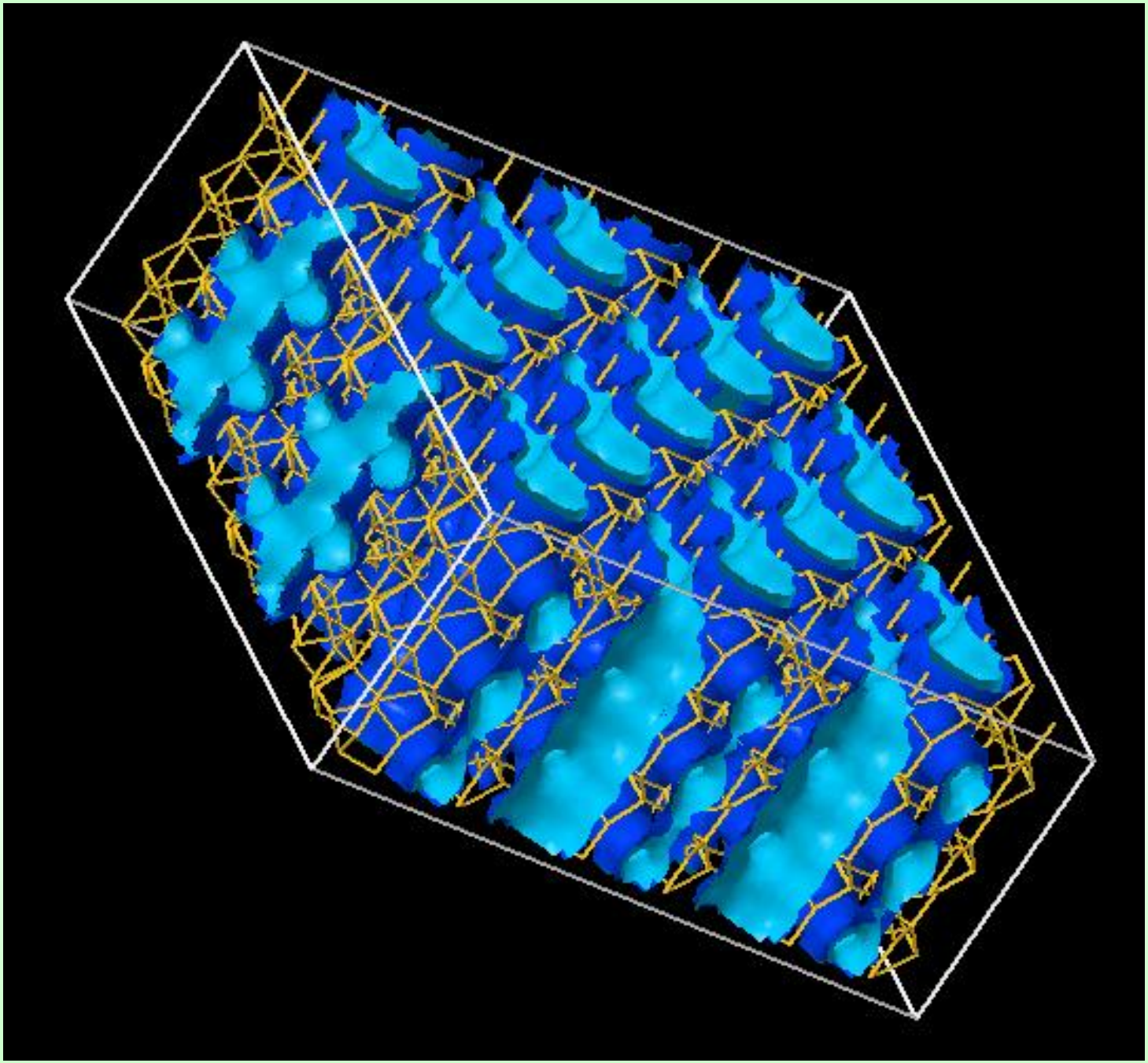
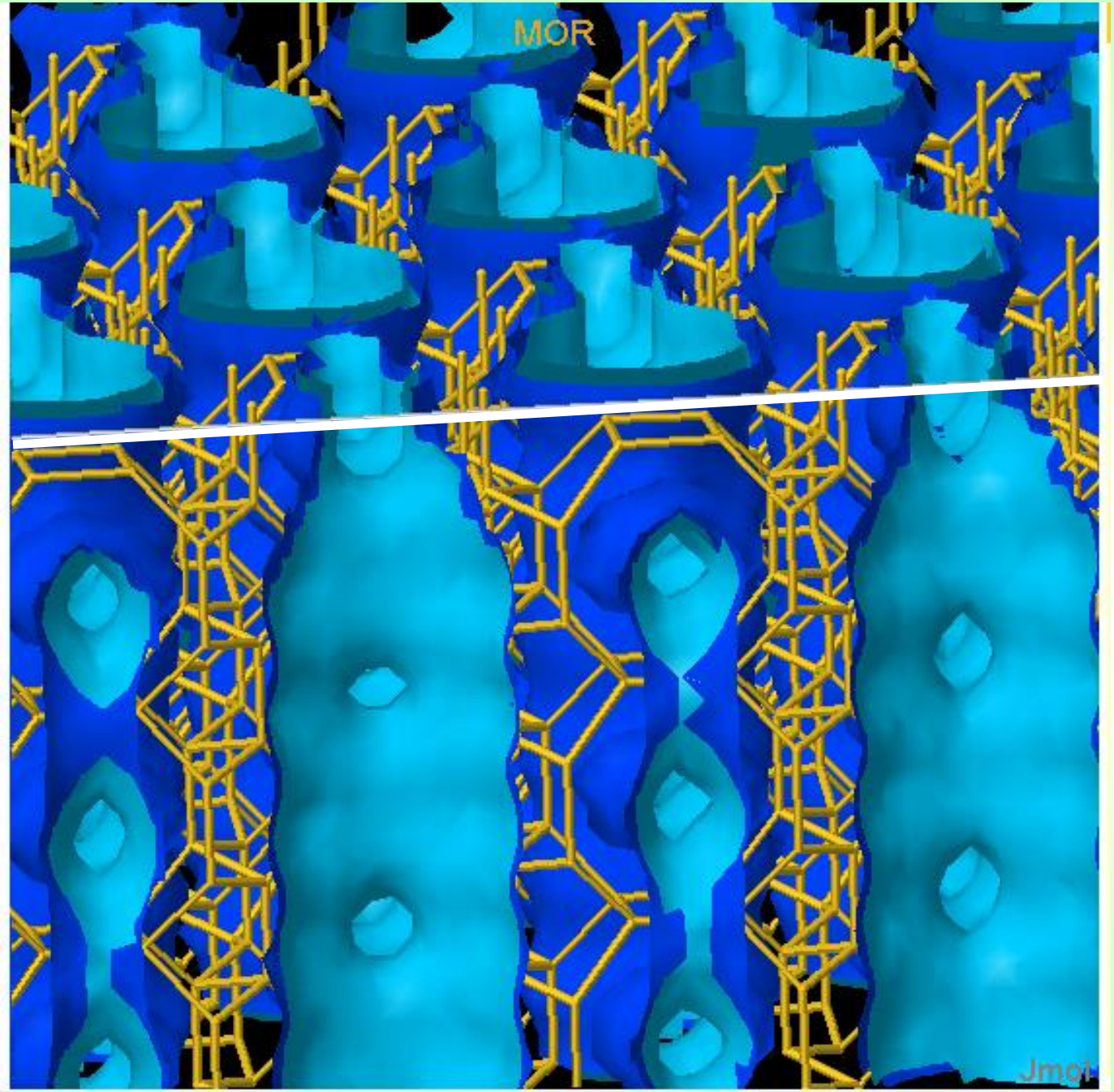
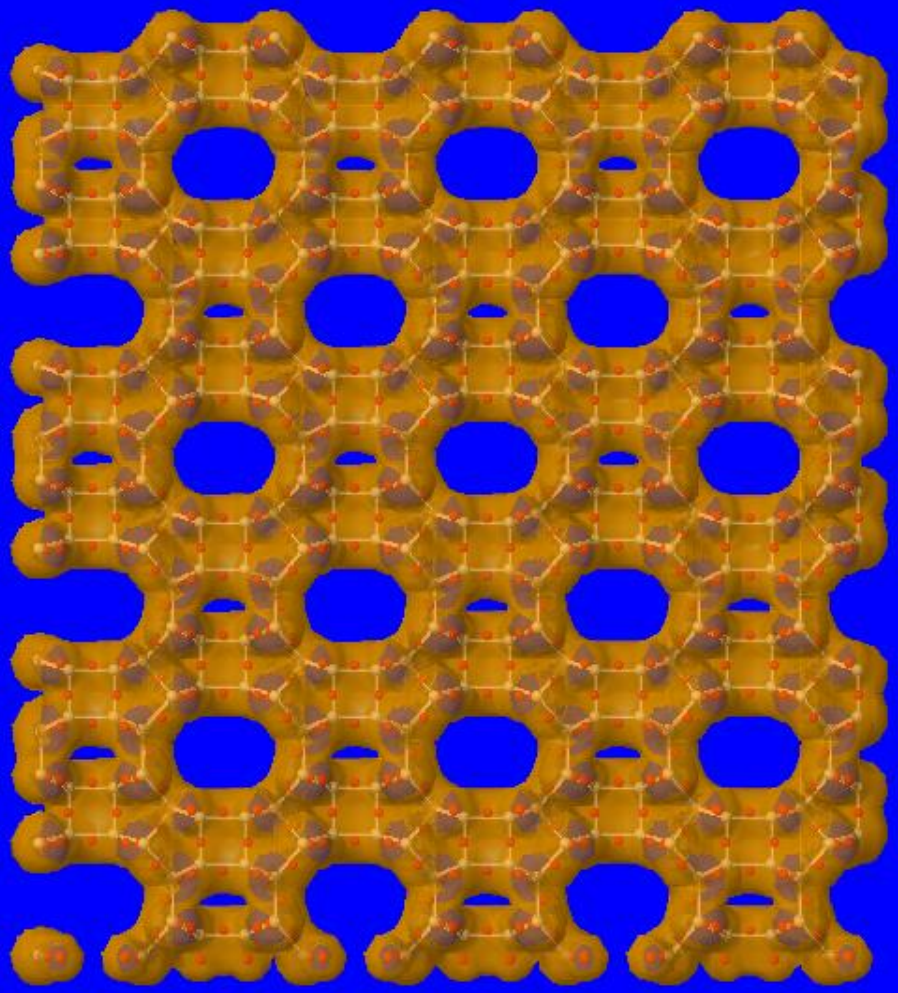
- Let's look at an example of such a zeolite as mordenite, on its interior space:



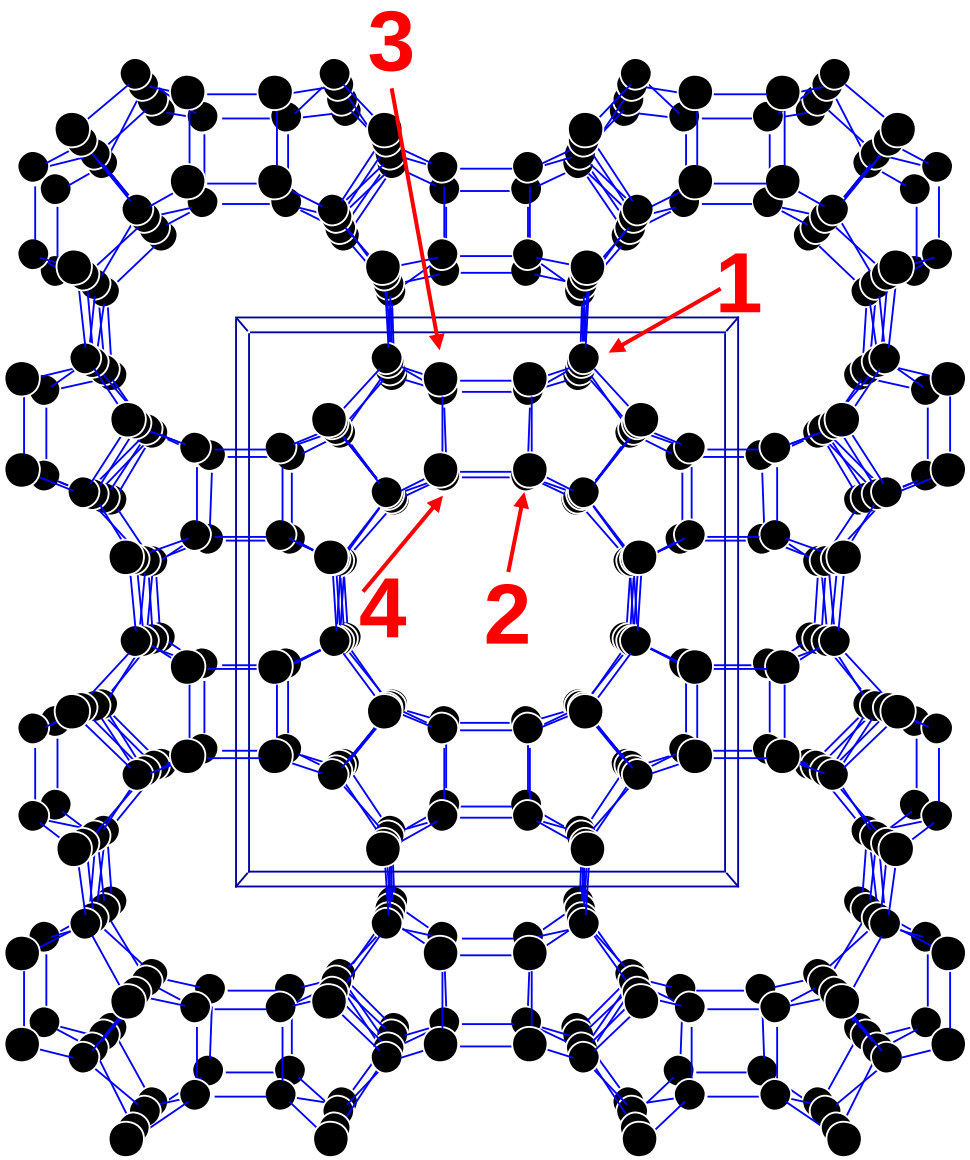

MOR
Jmol

MOR



Crossections of channels:

6.5 X 7.0 Å
2.6 X 5.7 Å



There are four inequivalent sites of T-atoms in the crystalline structure, labeled as T1-T4, with relative populations as 16:16:8:8.

Si atoms con occupy any of these.

Al atoms can occupy sites T3 and T4 only.

Crystal structure of mordenite

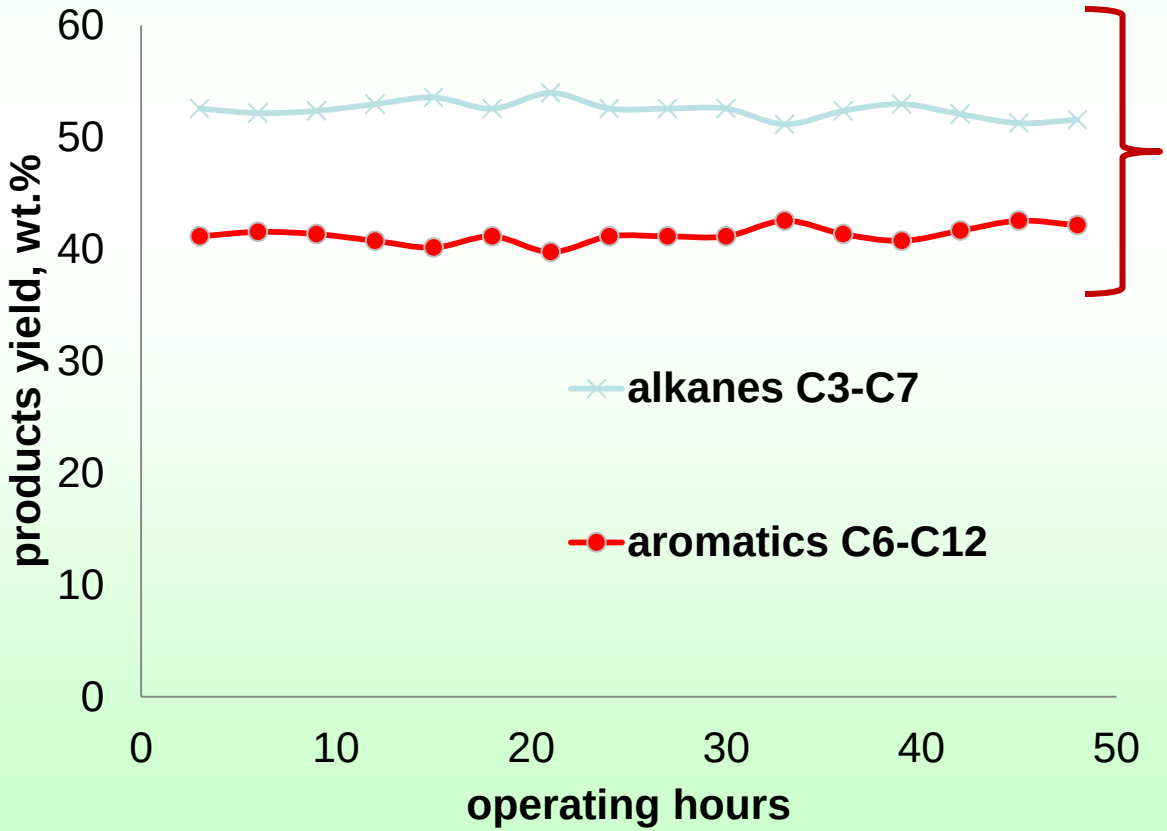
General opinion

- Zeolites are porous crystalline solids whose pores are of molecular dimensions thereby providing size and shape selectivity for guest molecules. Zeolites are widely used in catalysis as well as in the separation and purification fields due to:
  - ***their uniform, small pore size,***
  - ***high internal surface area,***
  - ***ion exchange properties,***
  - ***flexible frameworks, and***
  - ***controlled chemistry.***

Role of support in catalysis
1- Pd-Zn/Al_2O_3 2- Pd-Zn/MFI/Al_2O_3

1. Pd-Zn/Al_2O_3 - loss selectivity after 6 h

2.Pd- Zn/ZSM-5/Al_2O_3 - stable and selective during prolong test



Aim fraction of hydrocarbons C3-C12

- So, the list of miraculous properties of the zeolites:

  - *their uniform, small pore size,*
  - *high internal surface area,*
  - *ion exchange properties,*
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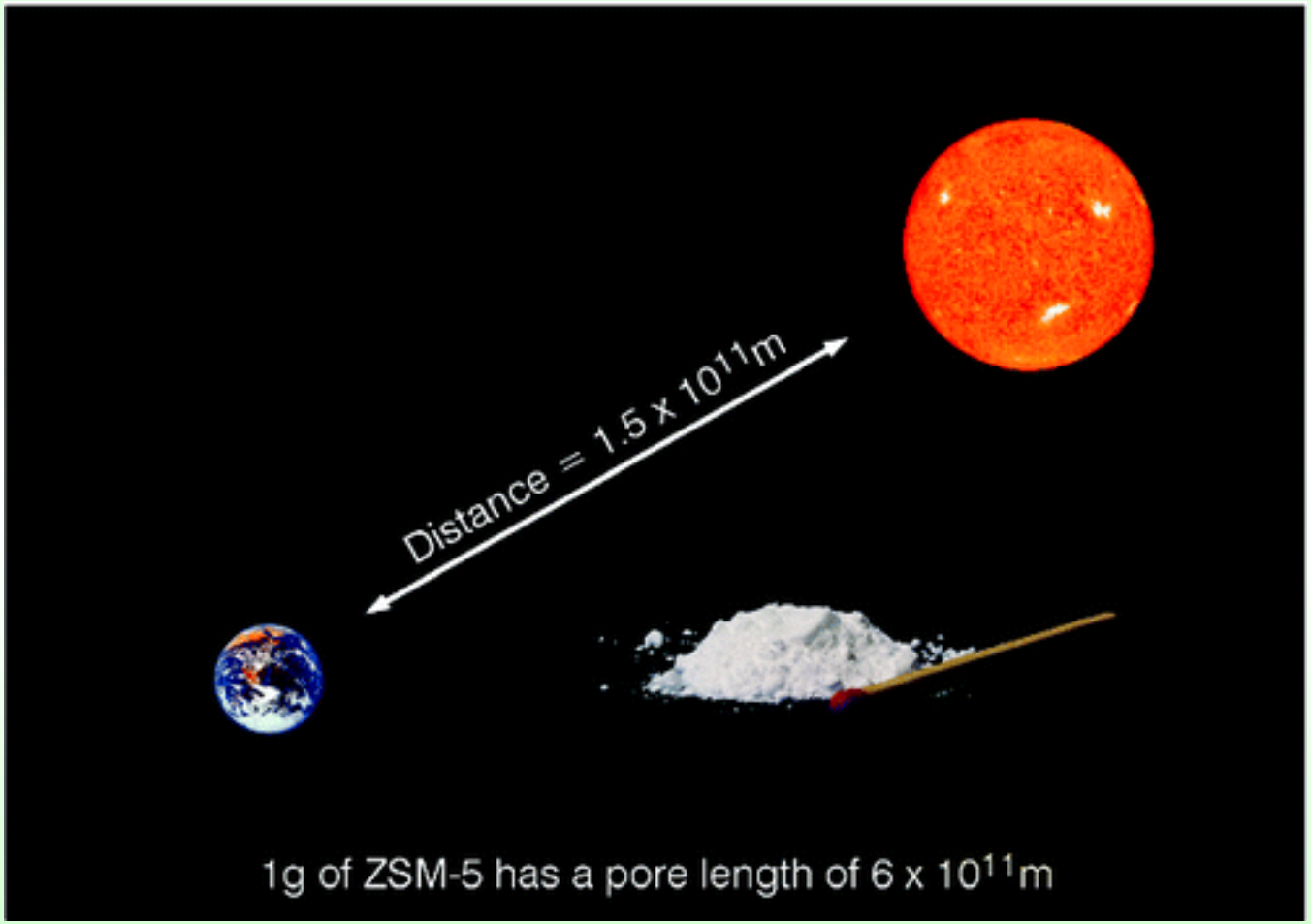
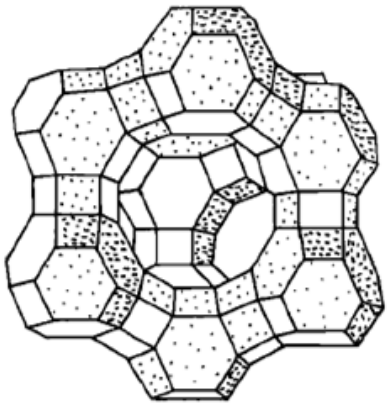
  - *controlled chemistry.*

1. Their porosity is the element of their crystal structure that makes it uniform in size. Their channels and cavities are so uniform, that they really start to act as the "molecular sieves“.

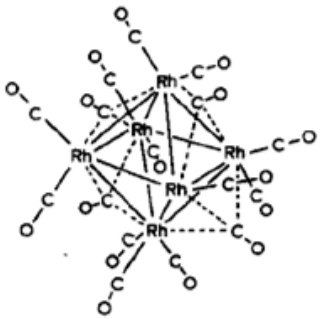
- But, this tiny diameters are the heavy problem if the size of reagents and products start to be bigger.



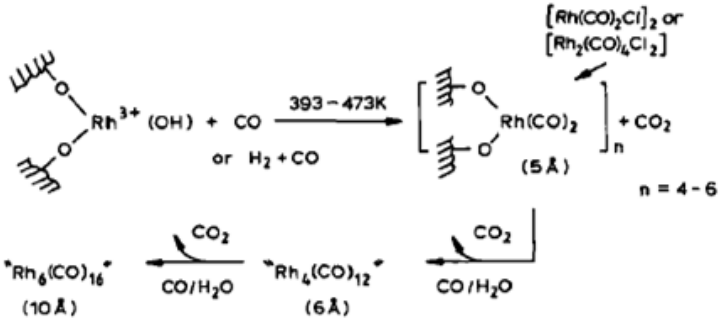
Representation of "ship-in-bottle" synthesis of $Rh_6(CO)_{16}$ metal clusters in NaY cages by the successive carbonylation of Rh^{3+} ions with $CO + H_2O$ or $CO + H_2$ as the building blocks, introduced by ion-exchange and admission of gas. O is attached to the zeolite wall

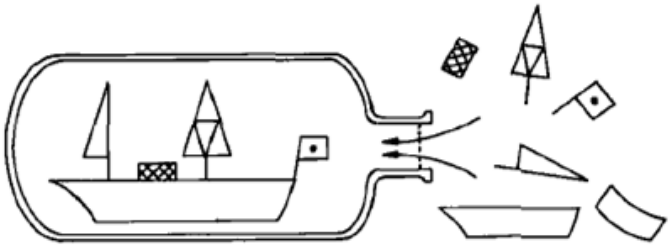


NaY zeolite, $SiO_2 : Al_2O_3 = 5.6$

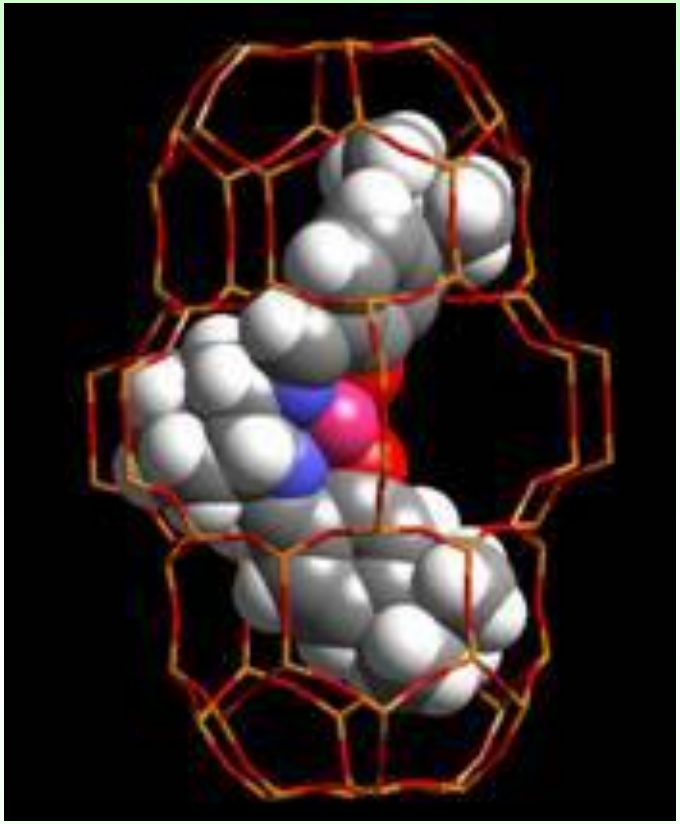


$Rh_6(CO)_{16}$

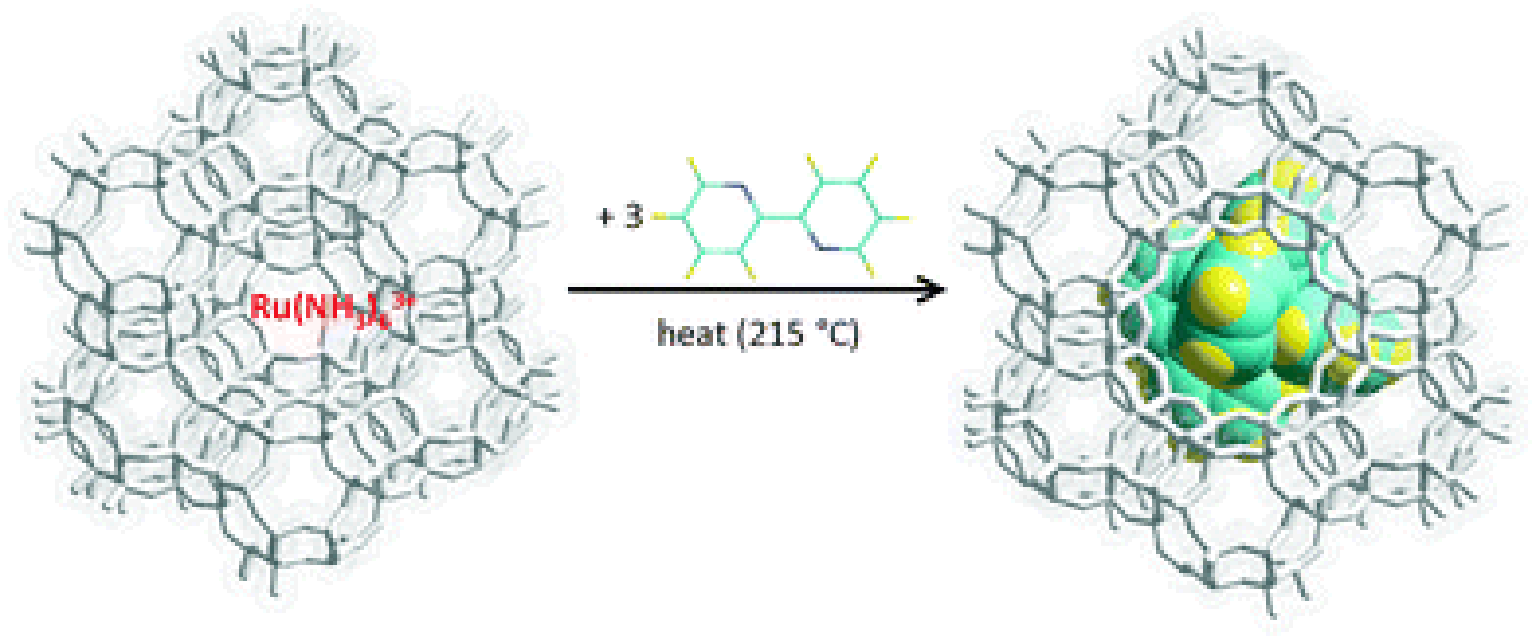




Ship-in-bottle



- Encapsulation of chiral metal complex in MCM-22, “ship-in-a-bottle complex”.

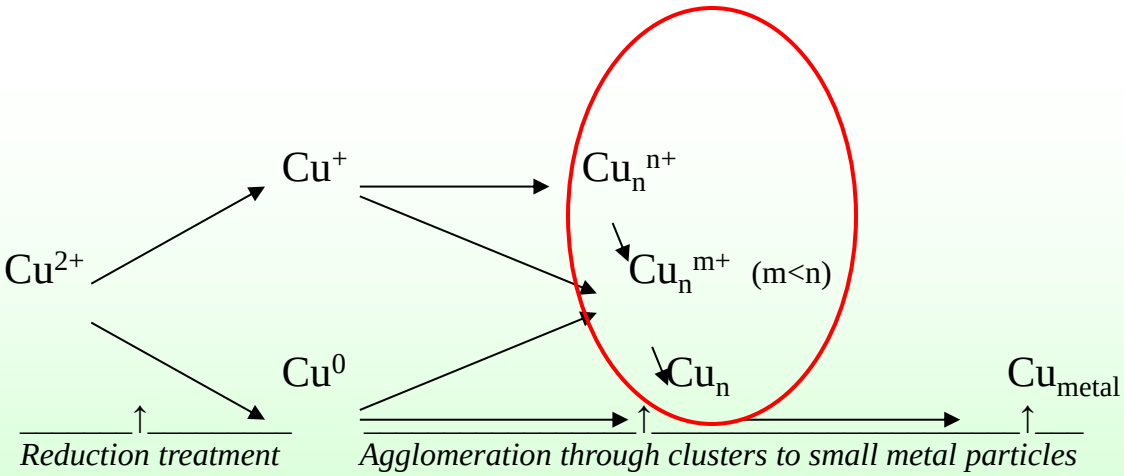

Ru(NH3)6 3+
+ 3
heat (215 °C)

- The most used way of introducing of the required reagents for synthesis of nanoparticles of selected compound is the use of ion exchange properties of zeolites.

The studies about metal particles implantation in zeolites are stimulated by their potential capacity for applications in the catalysis and medicine fields.

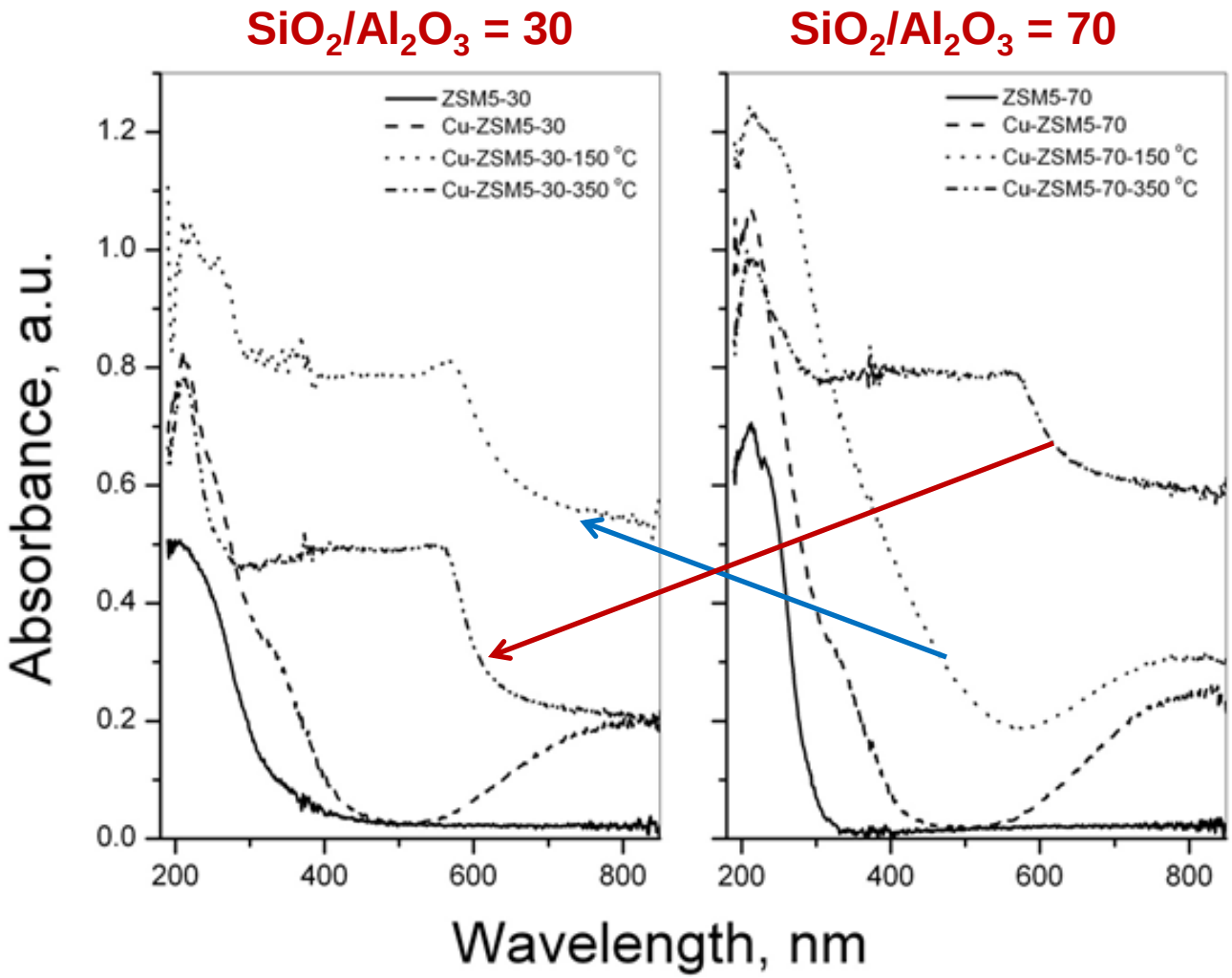
These qualities are sensitive to the state of metal, and this states in turn depends on the properties of matrix.

For example, stages of copper nanoparticles formation:



Schematic representation of chemical processes during reduction of Cu^{2+} ions to Cu metal particles

Influence of zeolite molar ratio on reducibility of Cu ions



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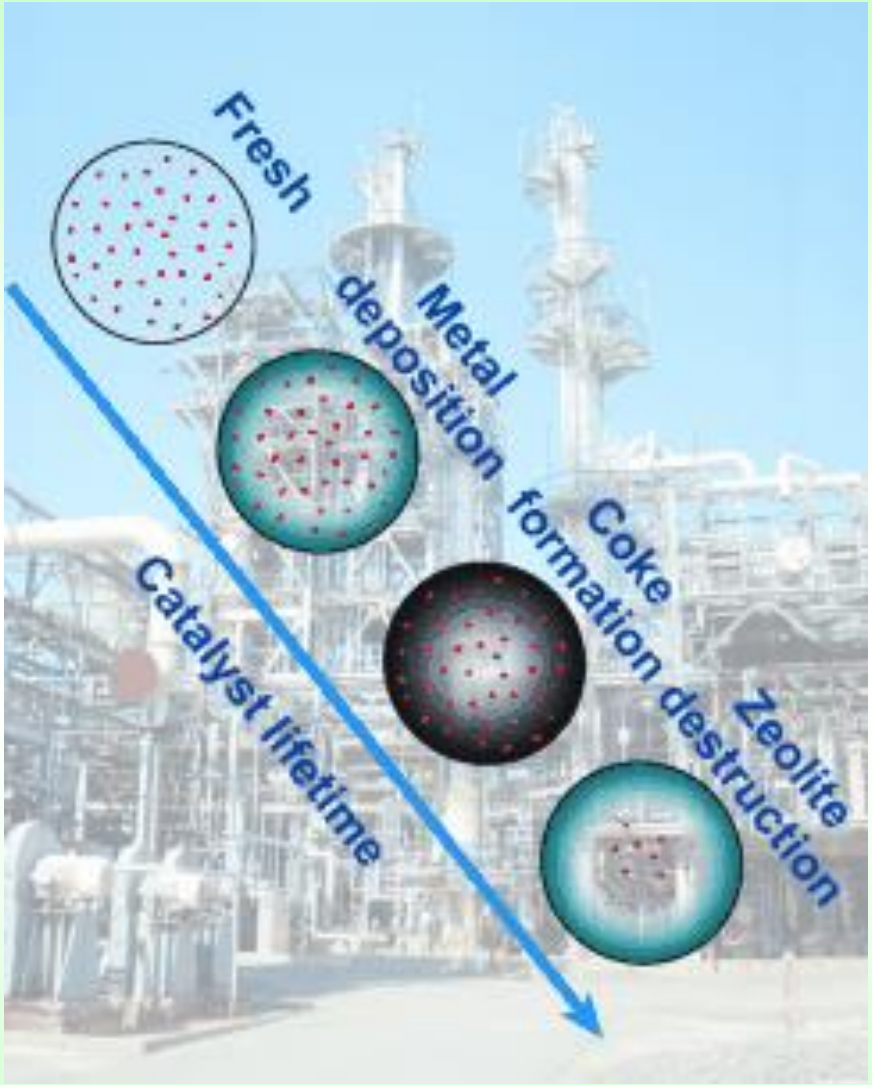
- However:
  - not all elements of the Periodic Table exist in solution as cations.
  - Also, the zeolites are sensitive to changes in pH.

Therefore, the ion exchange may proceed parallel to the processes of aluminum and/or silicon leaching from the zeolite structure, generating in this way new elements of porosity in solid materials structure.

- **Fluid catalytic cracking** (FCC) is the main conversion process used in oil refineries. Metal poisoning and related structural changes in the zeolite active material lead to a non-uniform core–shell deactivation of FCC catalyst particles.



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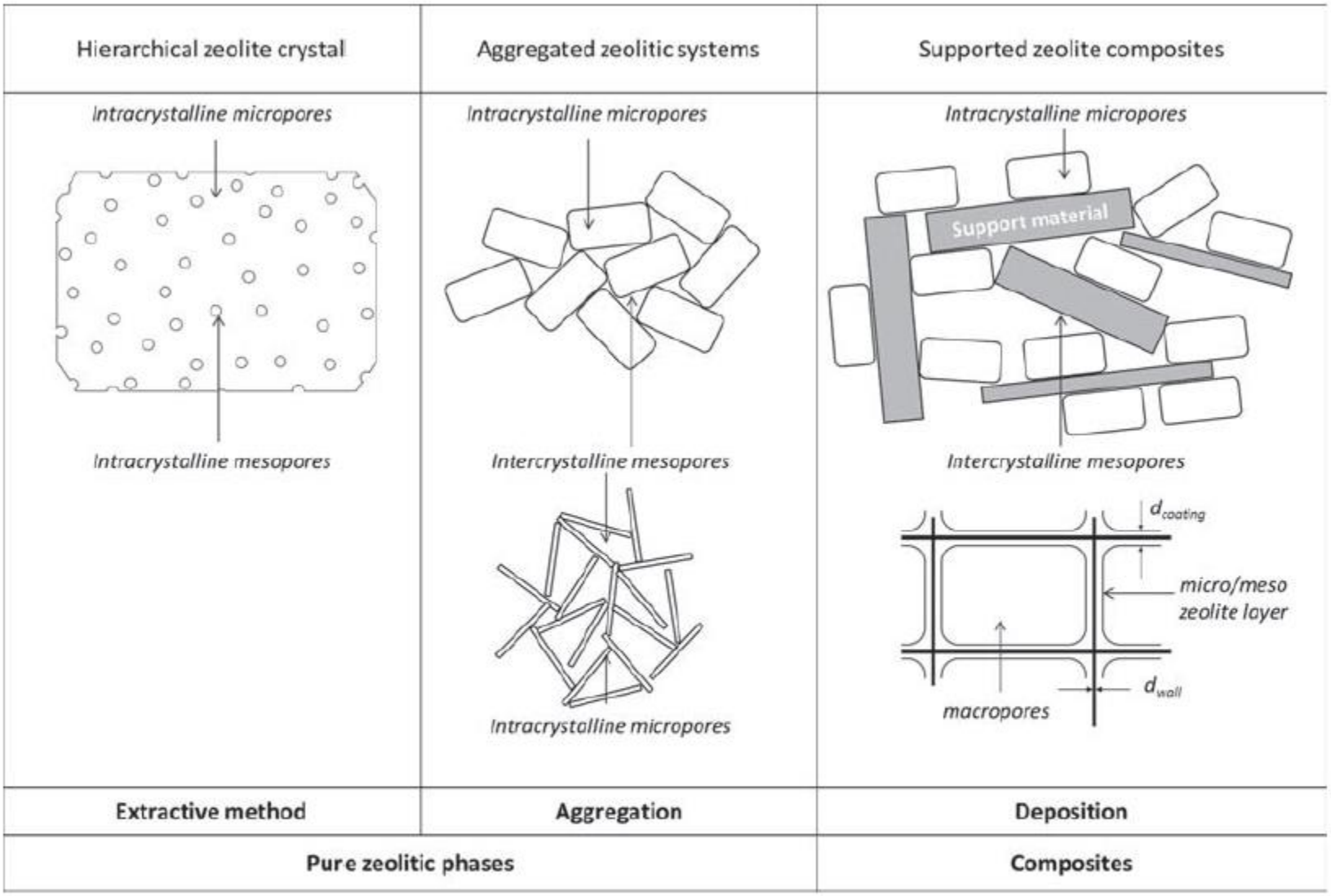
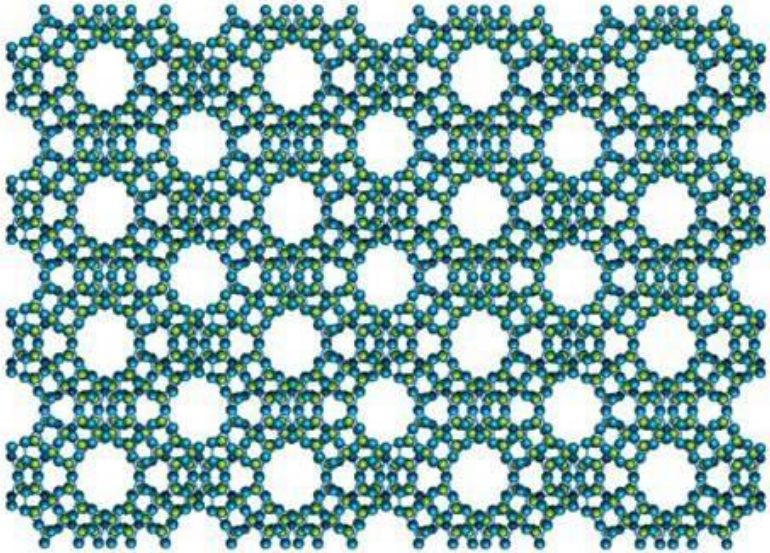
- “Mesopore-Modified”, or “Hierarchical” Zeolites:
  - The major drawback of zeolites is that the small size of the channels (less than 0.8 nm) and cavities (typically < 1.5 nm) imposes diffusional limitations on reactions that can cause high back pressure on flow systems.
  - It has been repeatedly demonstrated that mass transfer limitations play an important role in industrial applications using zeolites. To circumvent the diffusional limitation imposed by zeolitic structures, several potential solutions have been explored.
    - making zeolites with larger pores;
    - making smaller zeolite particles;
    - inserting larger pores into the zeolite particles.

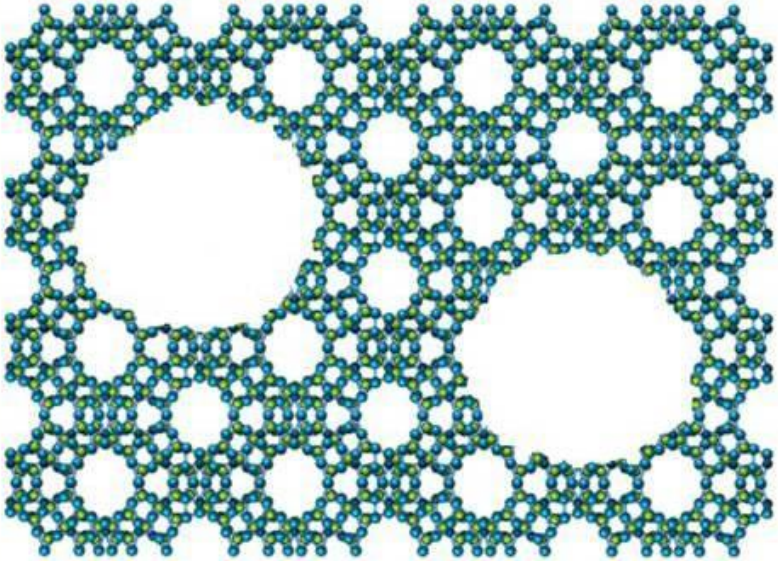


Extended classification of hierarchical zeolite materials according to the origin of the additional porosity

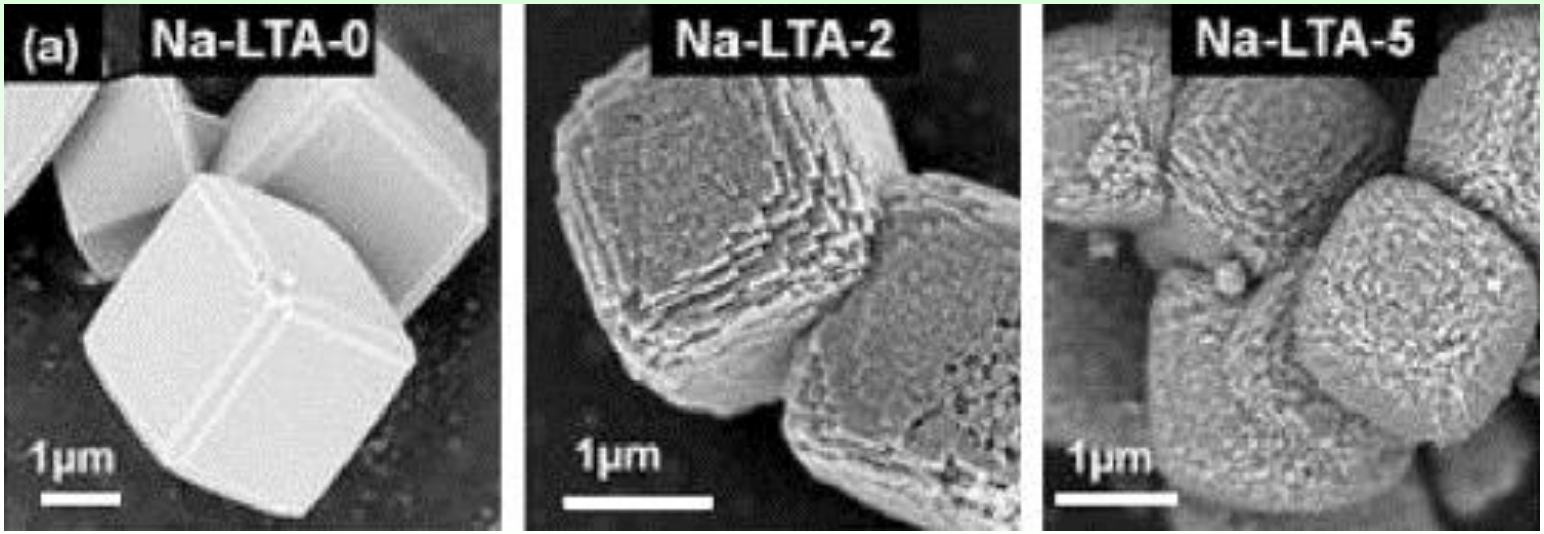
Adv. Mater. **2011**, *23*, 2602–2615

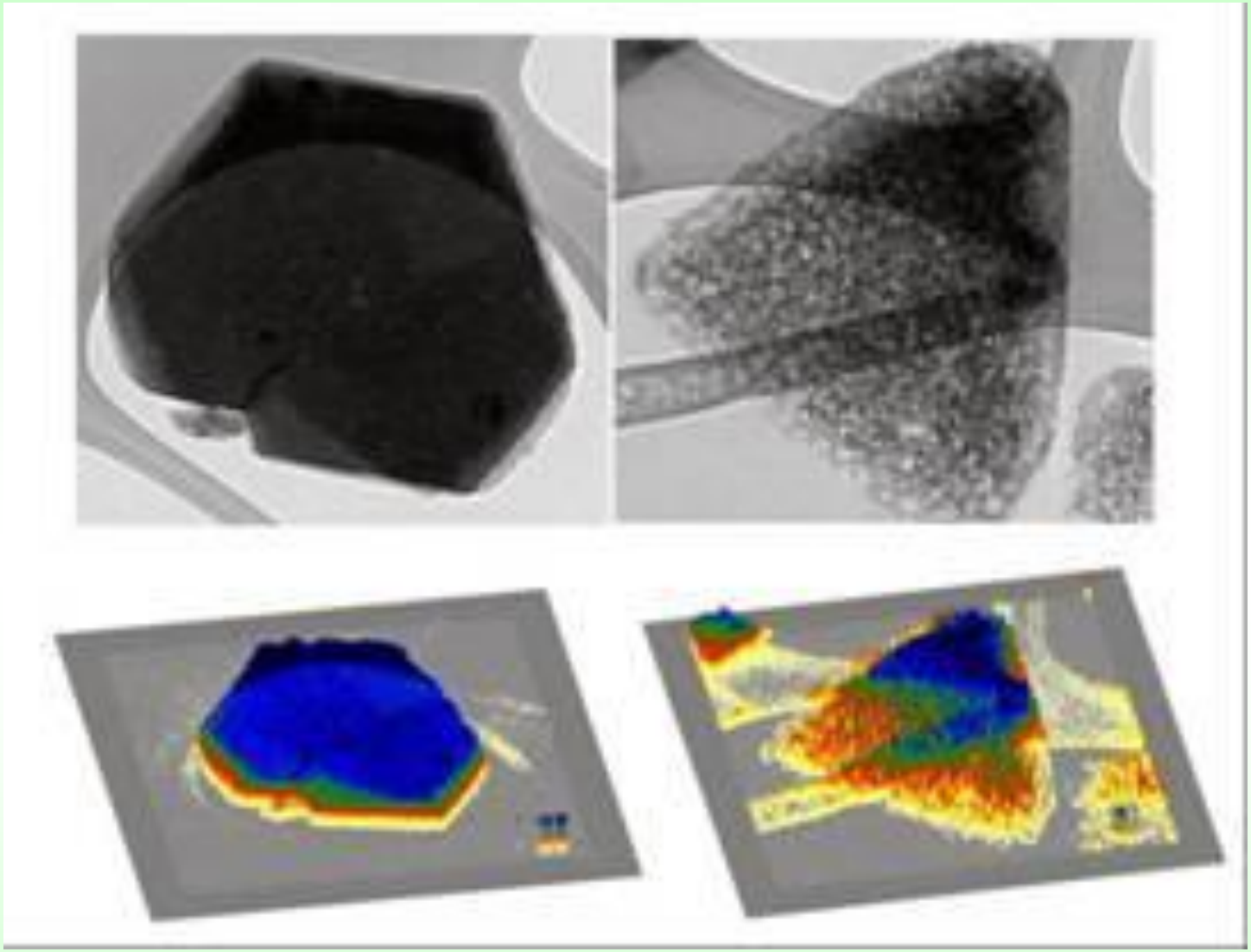


Conventional zeolite

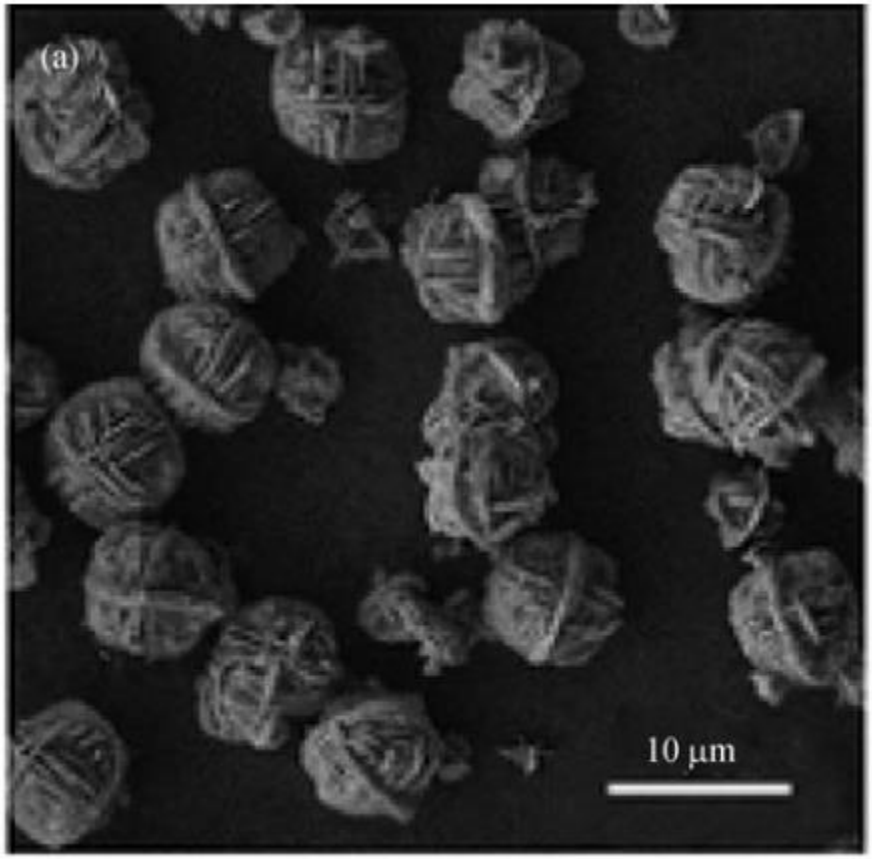


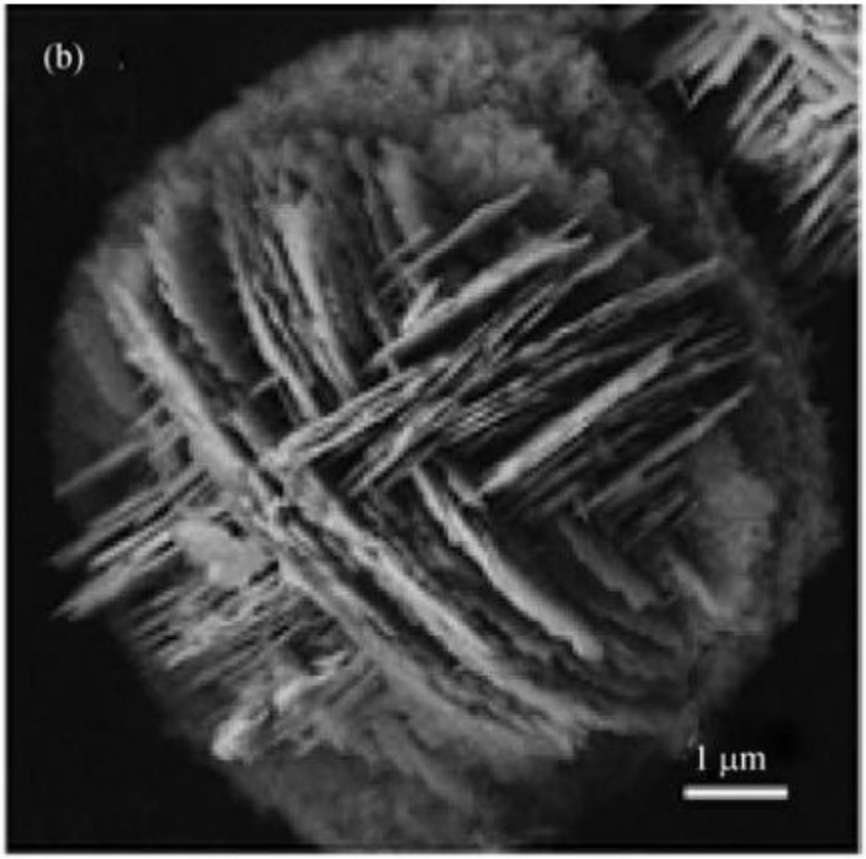
Zeolite with molecular highways


(a)
Na-LTA-0
1μm
Na-LTA-2
1μm
Na-LTA-5
1μm

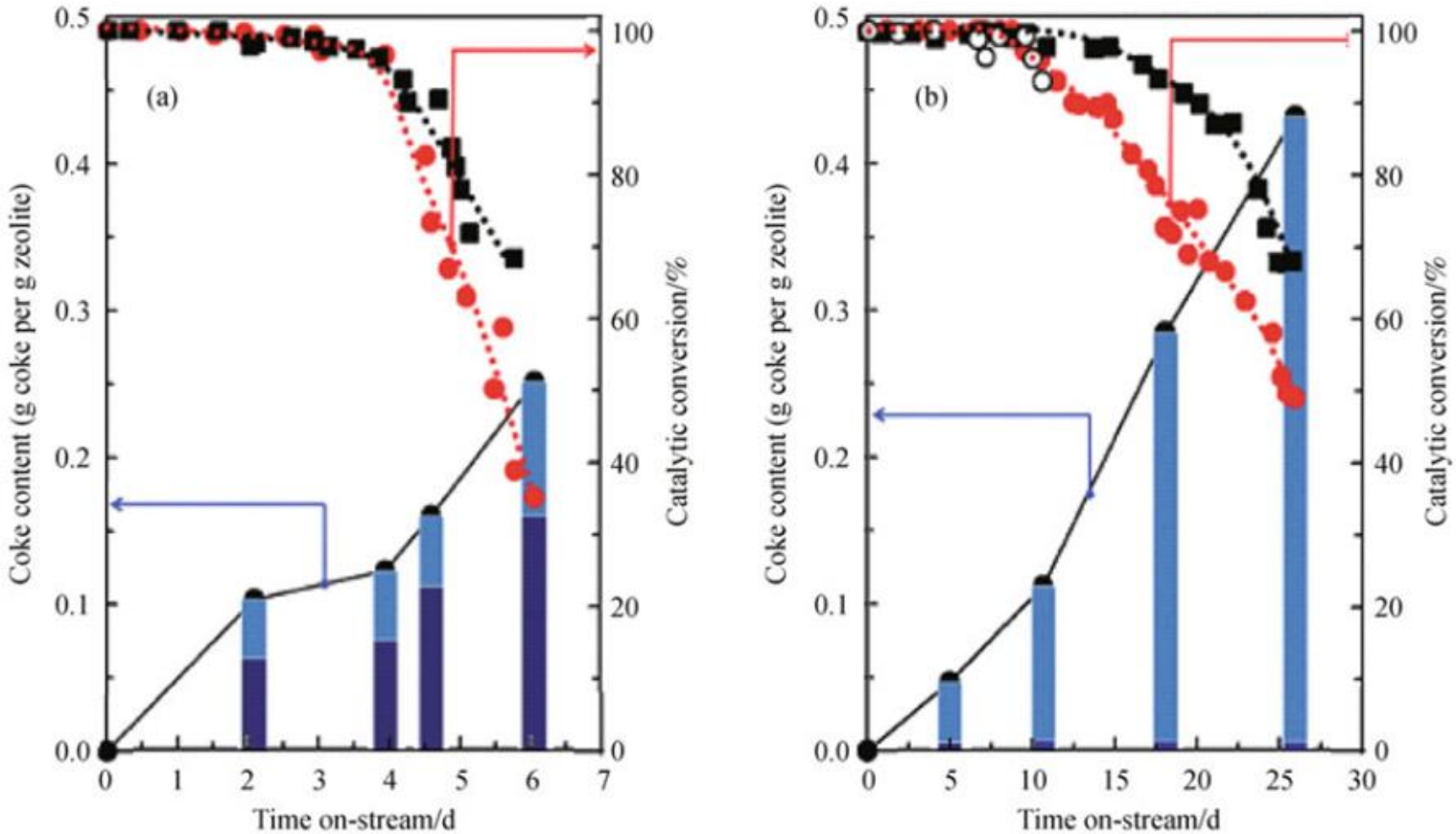


Y USY

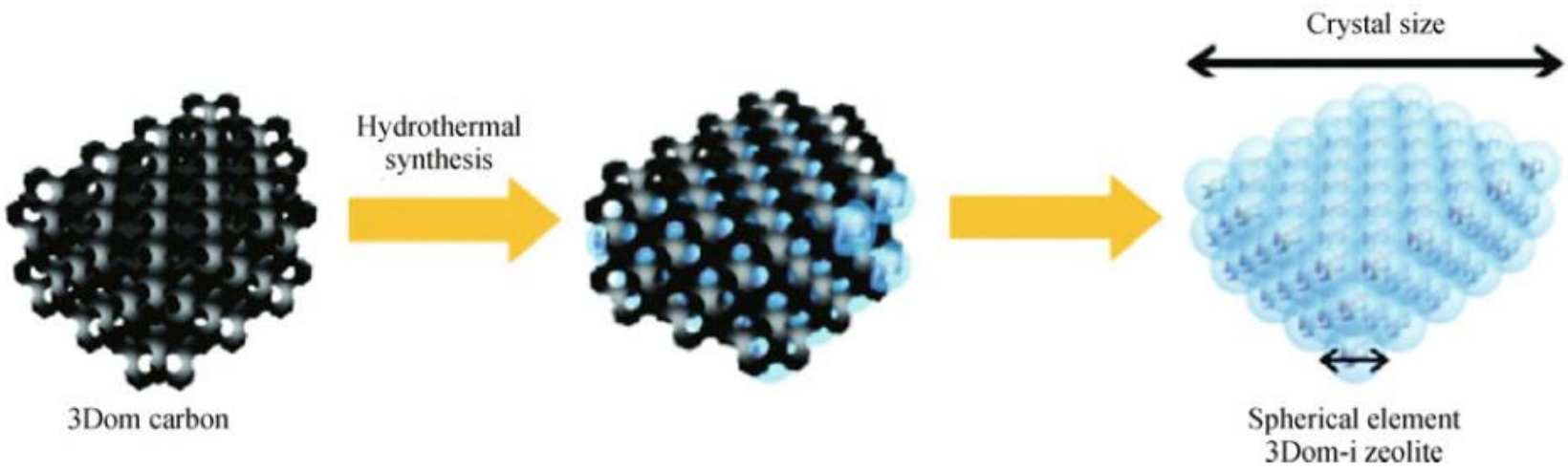

(a)
10 μm


(b)
1 μm

Front. Chem. Sci. Eng. 2013, 7(2): 233–248



Coke deposition over (a) conventional MFI zeolite and (b) unilamellar MFI zeolite catalysts during MTG conversion. Catalytic conversion over the unilamellar MFI was repeatedly investigated using three different synthesis batches (red circles, black squares, open circles, respectively). The catalytic measurement for conventional zeolite was repeated twice using the same sample (red circles and black squares). The solid black lines and the dotted red and black lines are guides to the eye. Dark blue bars indicate internal (inside the micropores of the zeolite) coke content, and light blue bars indicate external coke content.



Schematic illustration of 3Dom-i zeolite templating from 3Dom carbon.

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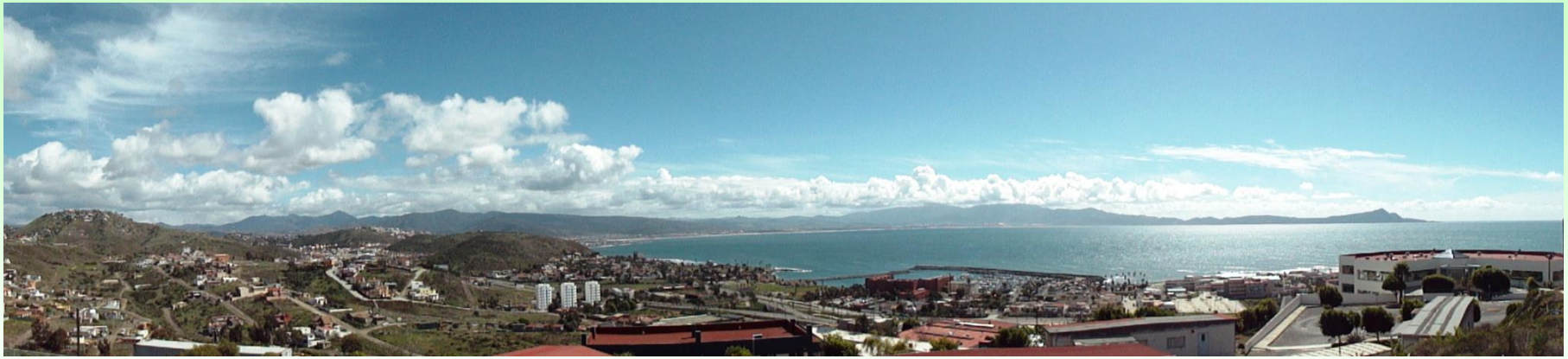
- Conclusion:

  That value, which is traditionally regarded as a positive feature of the system under certain conditions may easily be a drawback. Conversely, careful account of the properties of the system allows you to turn negatives into positives.



Gracias a todos por su atención