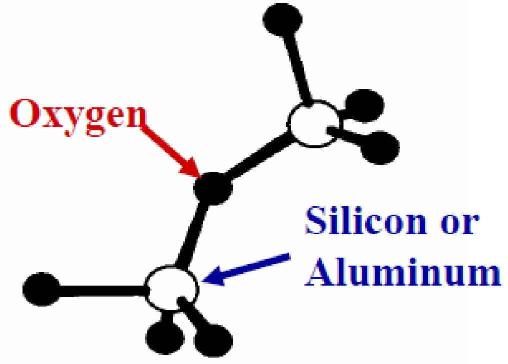
3.1. Introduction of Zeolite

What is zeolite?

- ✓ Greek derivation (zein,“to boil”; lithos,“a stone”) means “stones that boil”.
- ✓ Crystalline Aluminosilicate
- ✓ Consist of Corner-sharing Tetrahedra, TO_4 (T=Al or Si)
- ✓ Uniform molecular size pores (10 – 20 Å diameter) running throughout the solid.
- ✓ 40 natural and 130 synthetic zeolites known
- ✓ Aluminosilicates based on rigid anionic framework with well-defined channels and cavities.

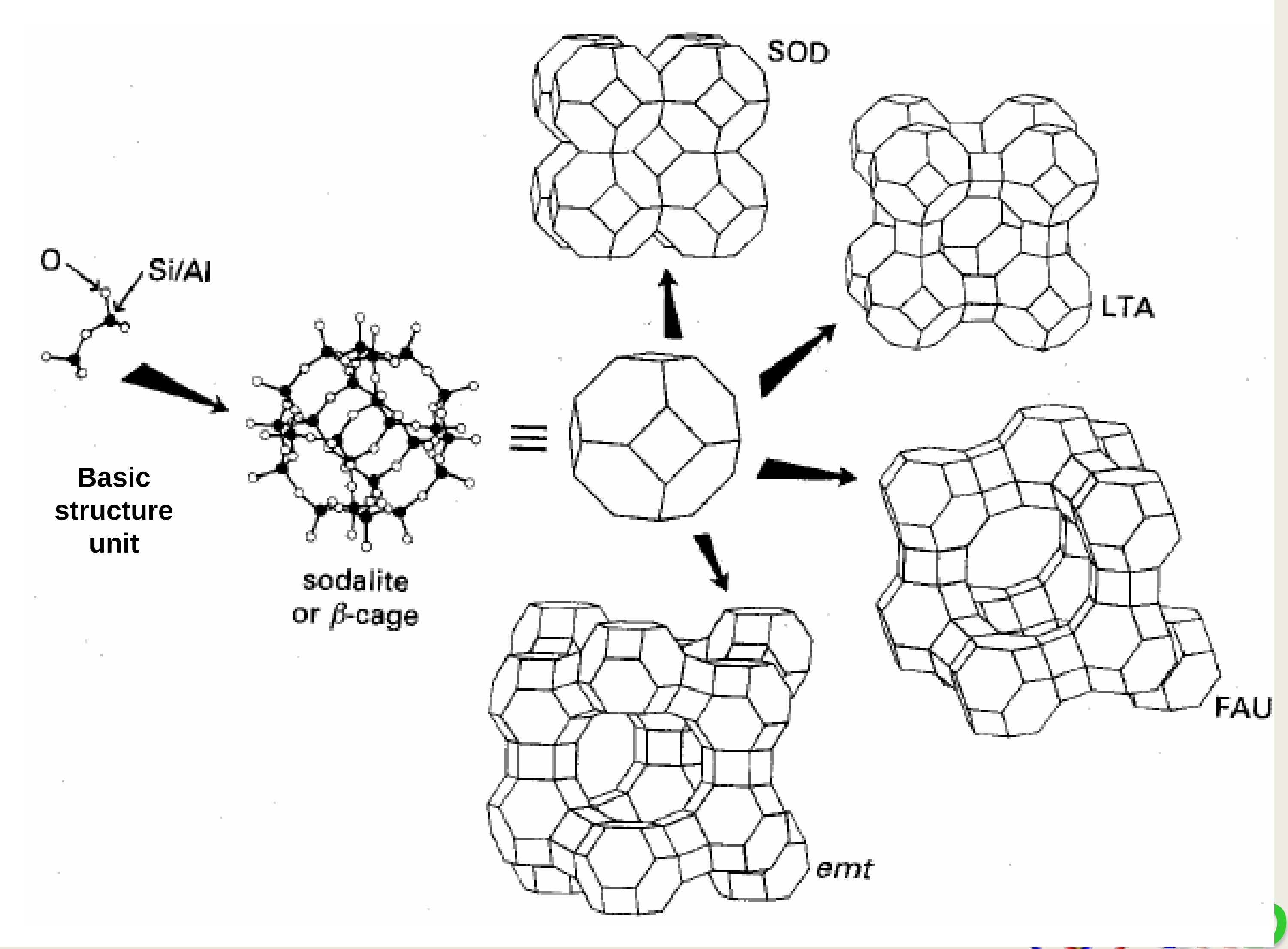


Corner-sharing TO_4
(T=Si or Al)

Introduction to Zeolite Science and Practice; Van Bekkum, H. et al. Eds; Elsevier: 1991.

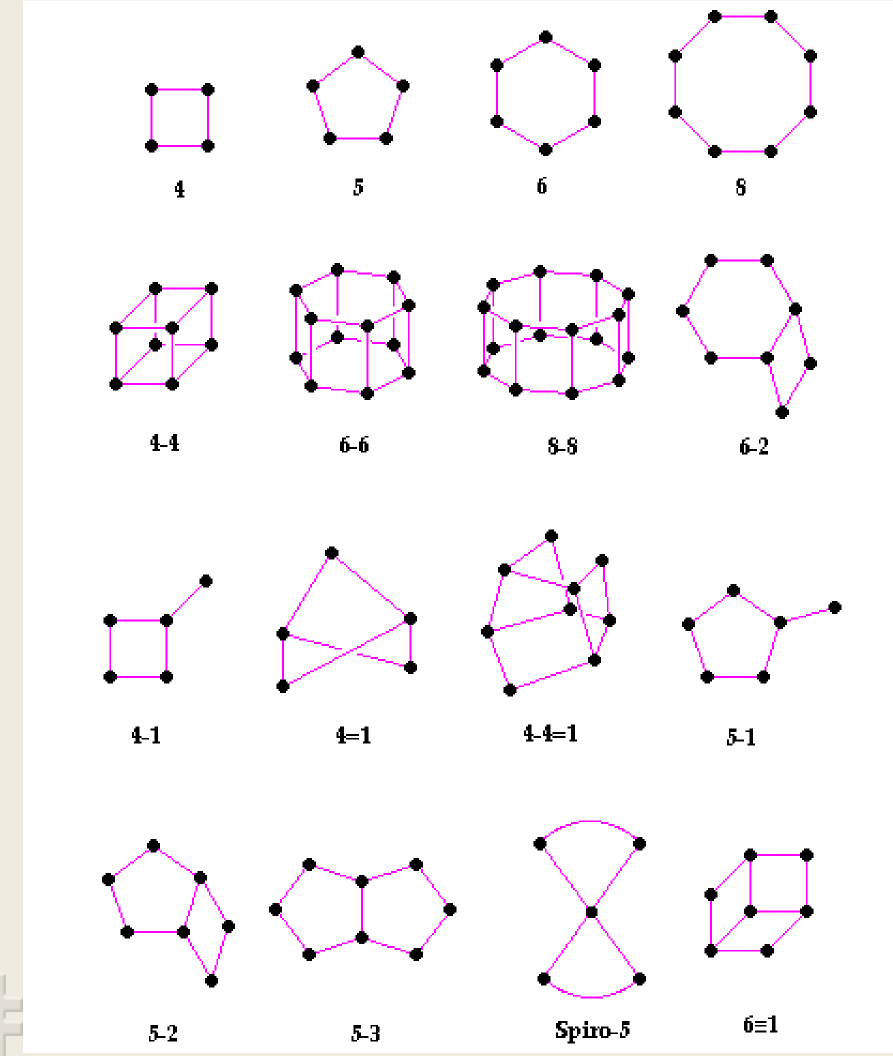
3.1. Introduction of Zeolite

Principle in zeolite construction (Self-assembly behavior)



3.1. Introduction of Zeolite

Secondary building units (SBU)



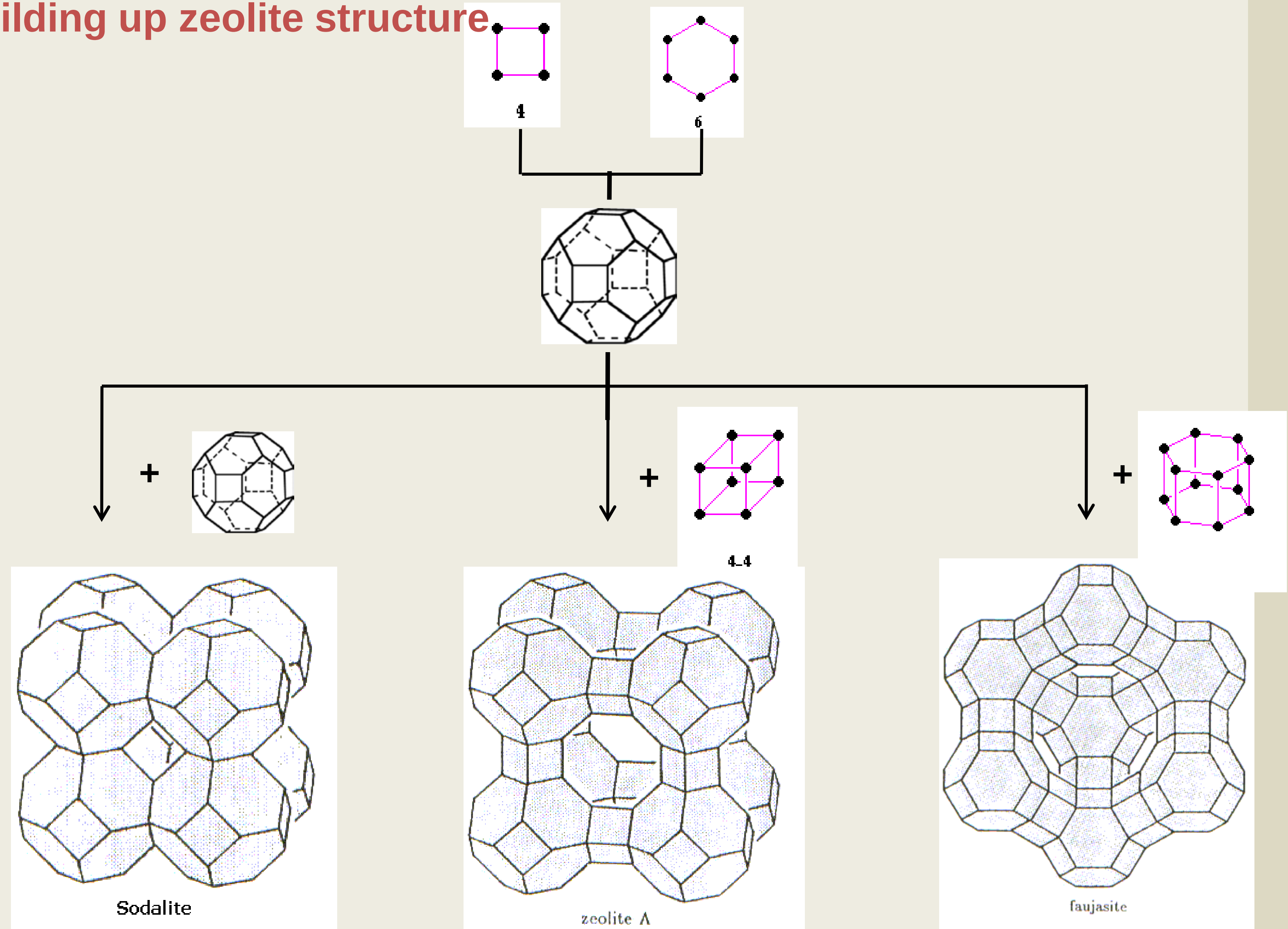
-The various zeolite structures can be classified according to their secondary building units (SBU)

- In the figure- the T atom of the TO_4 tetrahedron is located at each of the corners, and the oxygens are located towards the mid-points of the lines joining each T atom (*the oxygens are not shown to aid clarity*).

- These SBU can contain up to 16 T atoms. It can be noted that SBU's are non-chiral.

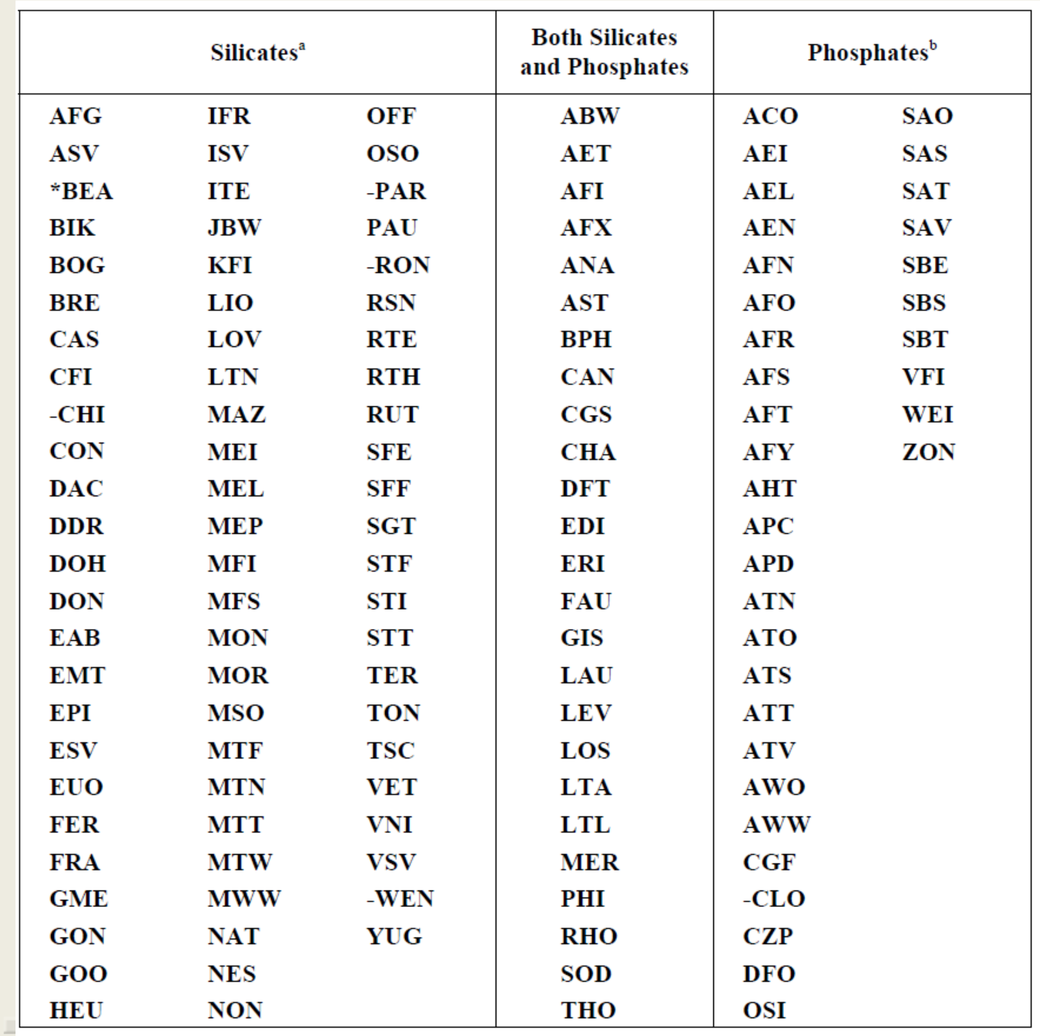
3.1. Introduction of Zeolite

Building up zeolite structure



3.1. Introduction of Zeolite

Structure Code



Silicates[a]			Both Silicates and Phosphates	Phosphates[b]	
AFG	IFR	OFF	ABW	ACO	SAO
ASV	ISV	OSO	AET	AEI	SAS
*BEA	ITE	-PAR	AFI	AEL	SAT
BIK	JBW	PAU	AFX	AEN	SAV
BOG	KFI	-RON	ANA	AFN	SBE
BRE	LIO	RSN	AST	AFO	SBS
CAS	LOV	RTE	BPH	AFR	SBT
CFI	LTN	RTH	CAN	AFS	VFI
-CHI	MAZ	RUT	CGS	AFT	WEI
CON	MEI	SFE	CHA	AFY	ZON
DAC	MEL	SFF	DFT	AHT	
DDR	MEP	SGT	EDI	APC	
DOH	MFI	STF	ERI	APD	
DON	MFS	STI	FAU	ATN	
EAB	MON	STT	GIS	ATO	
EMT	MOR	TER	LAU	ATS	
EPI	MSO	TON	LEV	ATT	
ESV	MTF	TSC	LOS	ATV	
EUO	MTN	VET	LTA	AWO	
FER	MTT	VNI	LTL	AWW	
FRA	MTW	VSV	MER	CGF	
GME	MWW	-WEN	PHI	-CLO	
GON	NAT	YUG	RHO	CZP	
GOO	NES		SOD	DFO	
HEU	NON		THO	OSI	

[a] including germanates

[b] including arsenates

Composition based classification

Origin of some code

✓ A- : the first synthesized

✓ ZSM : synthesized by Socony Mobil.

✓ LT- : synthesieze by Linde. (Linde Type-)

Atlas of zeolite structure types; Walter M. Meier. et al. Eds; Elsevier: 2001.

3.2. Properties and Applications of Zeolite

Representative properties

✓ The microporous character with uniform pore dimensions – allowing certain hydrocarbon molecules to enter the crystals while rejecting others based on too large a molecular size.

✓ The ion-exchange properties – allowing to perform all sorts of ion exchange reaction.

✓ The ability to develop internal acidity – making the zeolites interesting materials for catalyzing organic reactions

✓ Framework robustness and high thermal stability

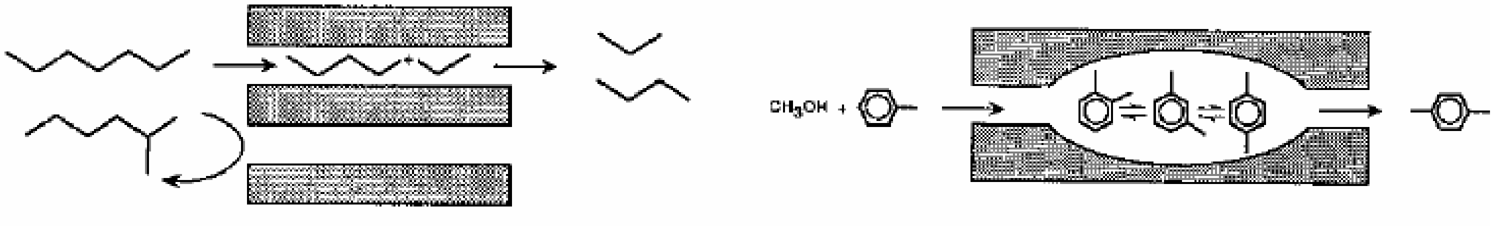
Introduction to Zeolite Science and Practice; Van Bekkum, H. et al. Eds; Elsevier: 1991.

3.2. Properties and Applications of Zeolite

Applications (Shape, Size selectivity)

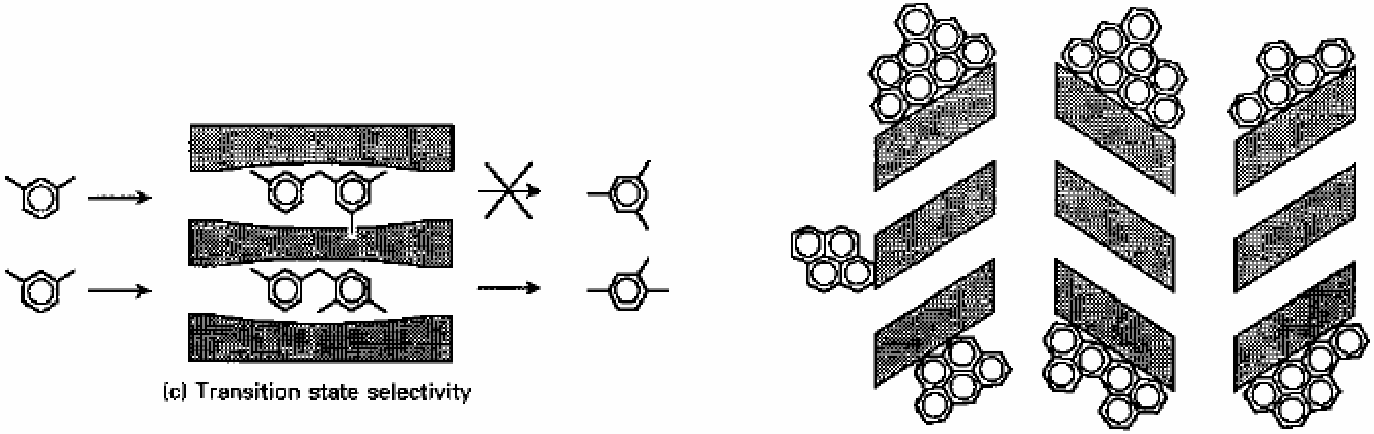
✓ Molecular sieves : Separation of straight & branched chain hydrocarbons, Separation of CO2 from natural gas

✓ Shape-selective catalysis: Reaction of methanol & toluene to form p-xylene selectively



(a) Reactant selectivity

(b) Product selectivity



(c) Transition state selectivity

(d) Exterior coke formation

3.2. Properties and Applications of Zeolite

Applications (Ion exchange)

✓ Zeolite usually contain cations (e.g., Na^+, K^+, or NH_4^+) after the synthesis.

✓ Cation exchange : radioactive decontamination, e.g. removal of Sr2+ and Cs+ from “dump waters” of nuclear power stations; industrial “water softeners”, to prevent lime-scale blocking up cooling pipes in manufacturing facilities; removal of heavy metals from the environment, e.g. lead, zinc, copper, mercury, cadmium

✓ Anion absorption. Environmental contamination by toxic anions may also be removed, by reaction with heavy metal cations previously exchanged into the zeolite

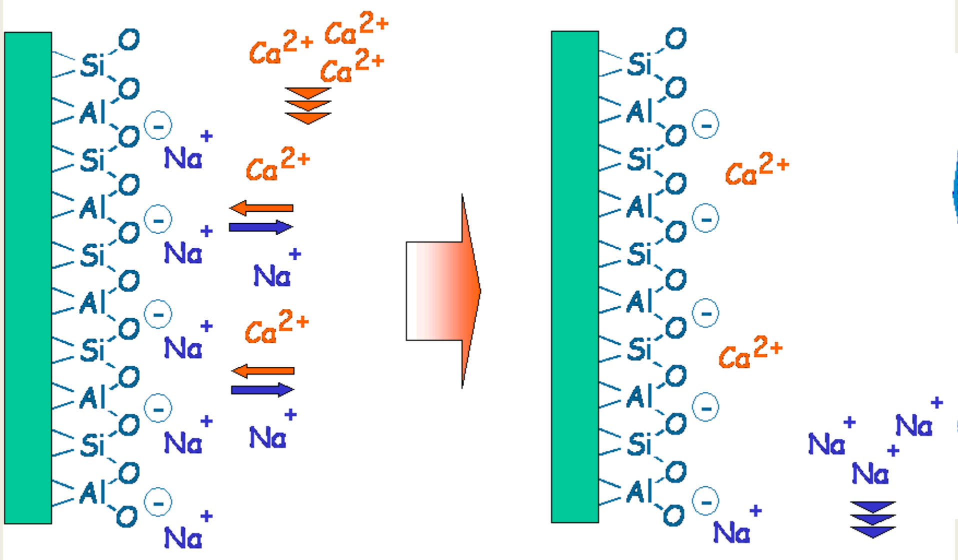


Fig. Ion-exchangers to remove cationic species from aqueous solutions by replacing them by sodium cations.

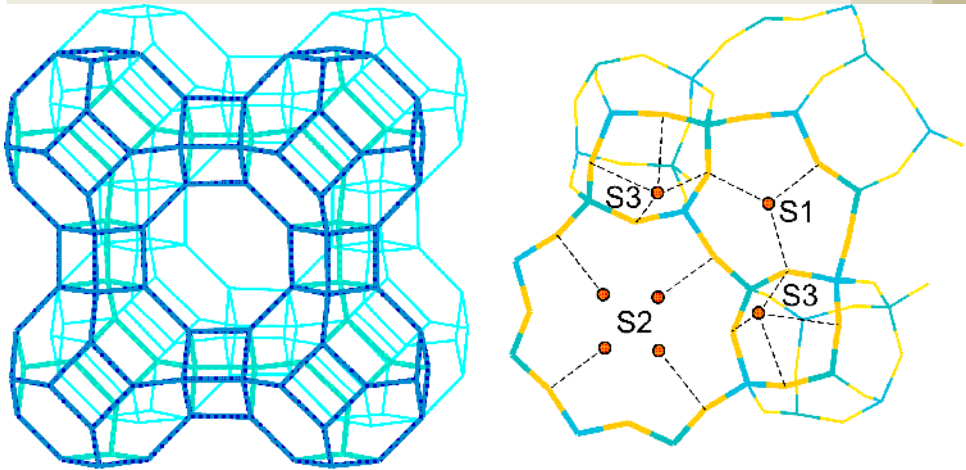


Fig. the most common cation sites in Zeolite A as an example

3.2. Properties and Applications of Zeolite

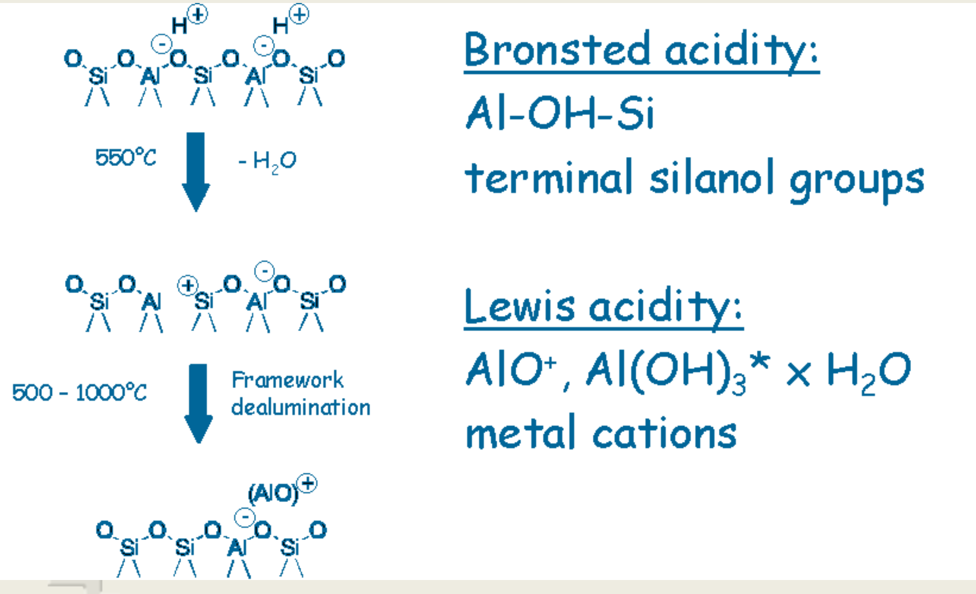
Applications (Acidity)

✓ Protonated zeolites have acidic properties.

✓ Reduction in NOx emissions from vehicles, using zeolite-loaded “catalytic converter”.

✓ Catalysts : petroleum refining, synfuel production, petrochemical production.

✓ p-xylene is needed for the production of polyesters - Xylenes can be rearranged over ZSM-5



Bronsted acidity:

Al-OH-Si

terminal silanol groups

Lewis acidity:

AlO^+, $Al(OH)_3$* x H_2O

metal cations

Fig. Acidity in zeolite

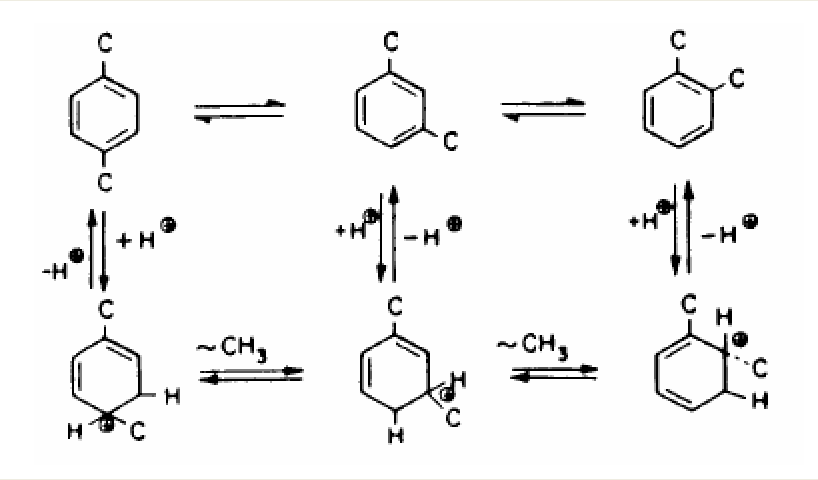


Fig. selectively obtained p-xylene

3.2. Properties and Applications of Zeolite

Applications (The others)

✓ Medical applications: Hemosorb and QuikClot are commercial products based on zeolites which when applied to wounds (in accidents or surgery) are said to cause an “instant” cessation of bleeding. Zeolites are also used in kidney dialysis machines, to absorb ammonia from blood and prevent it from building up in the body (a job that healthy kidneys normally do).

✓ Agriculture: for supplying K+ and NH4+ to plants from soils that have been enriched with zeolites exchanged specifically with these cations. It is suggested that such “zeoponics”, as the strategy is called, might be used to grow food on long space missions.

✓ Separation of gases: there are commercial units that can provide oxygen of 95% purity for use in hospitals or for patients e.g. suffering from emphysema and other forms of Obstructive Pulmonary Disease (OPD), by separating it from air. Nitrogen (80% of air) is preferentially absorbed over oxygen because of its much larger molecular electric quadrupole moment, and so enables oxygen to separate from air almost in a state of purity.

Annu. Rep. Prog. Chem., Sect. C, **2007**, 103, 287

3.3. Synthesis of Zeolites

Hydrothermal synthesis

✓ Most zeolites have been synthesized under hydrothermal conditions.
✓ 'hydros' in the Greek meaning water and 'thermos' meaning heat
✓ After Si and Al sources and mineralizers such as NaOH or KOH are mixed in water, the hydrogels obtained are heated at prescribed temperature and crystallized into zeolites

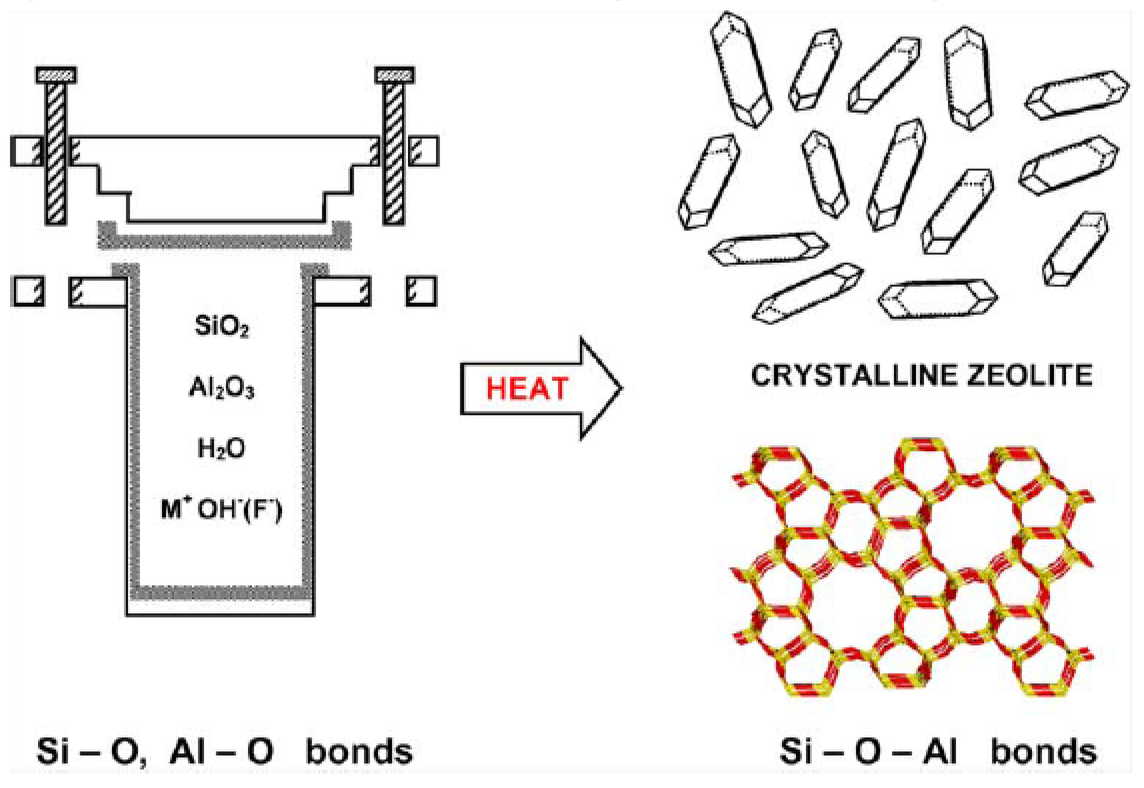
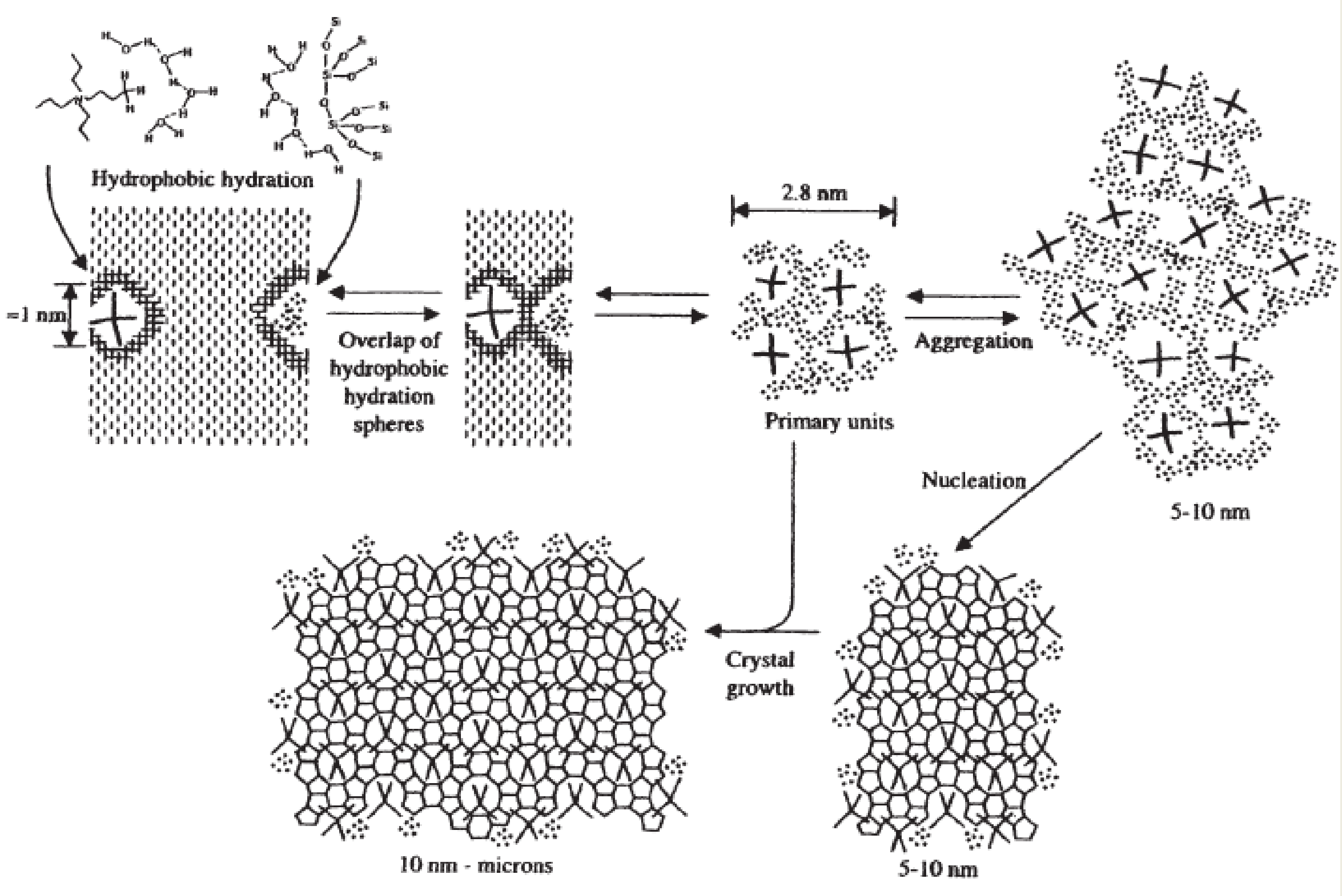


Fig. Hydrothermal reaction for synthesis of zeollite

Micropor. Mesopor. Mater. **2005**, 82, 1.

3.3. Synthesis of Zeolites

Overview of crystallization mechanism of zeolite



Chem. Lett. **2005**, 34, 276

3.3. Synthesis of Zeolites

The evolution of order

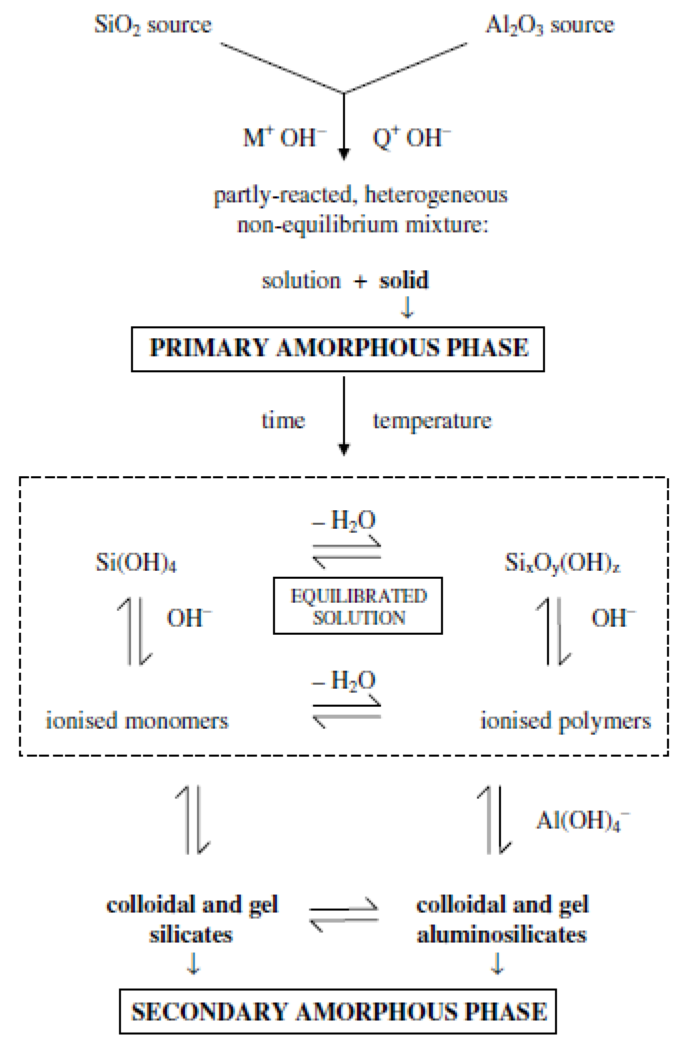


Fig. Equilibration of the starting mixture to establish a partly ordered intermediate (secondary amorphous phase) and a characteristic distribution of solution species.

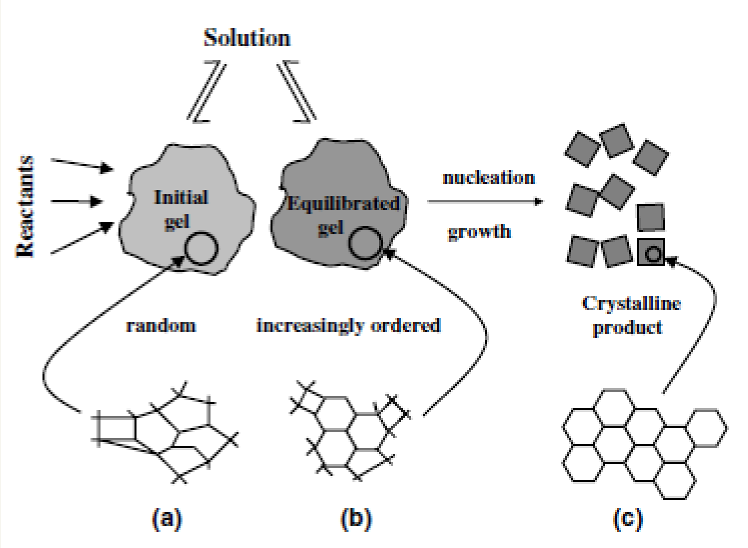


Fig. The evolution of order, from the primary amorphous phase (a) through the secondary amorphous phase (b) to the crystalline product (c)

Micropor. Mesopor. Mater. **2005**, 82, 1.

3.3. Synthesis of Zeolites

Nucleation

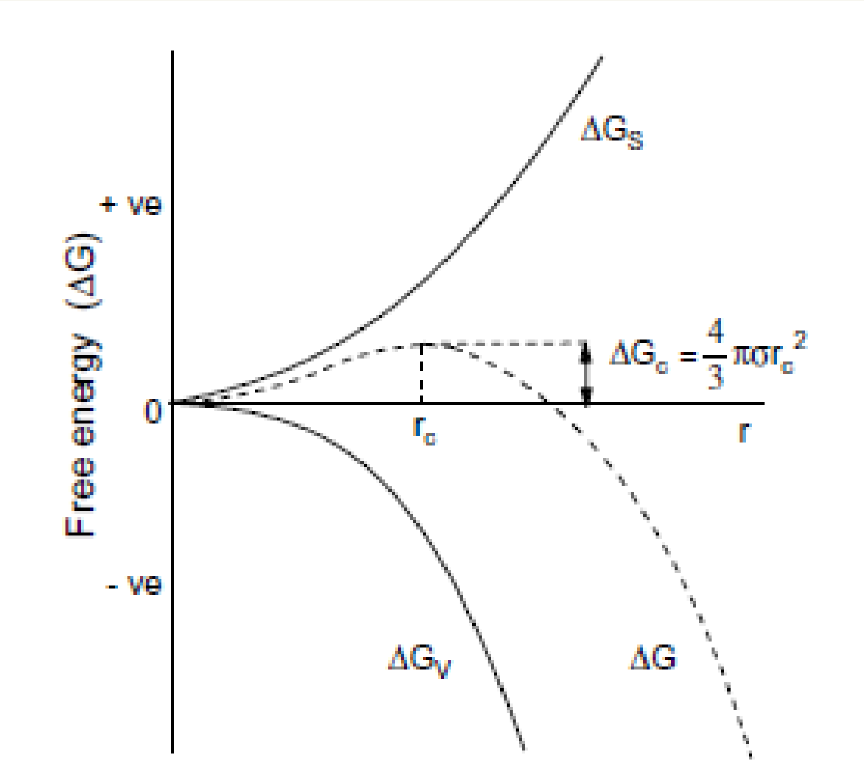


Fig. The energetics of nucleation, illustrating the concept of a critical nucleus of radius r_c; beyond this size, the net energy gain from the resultant (ΔG) of cohesive (ΔG_v) and surface (ΔG_s) terms is favourable to growth

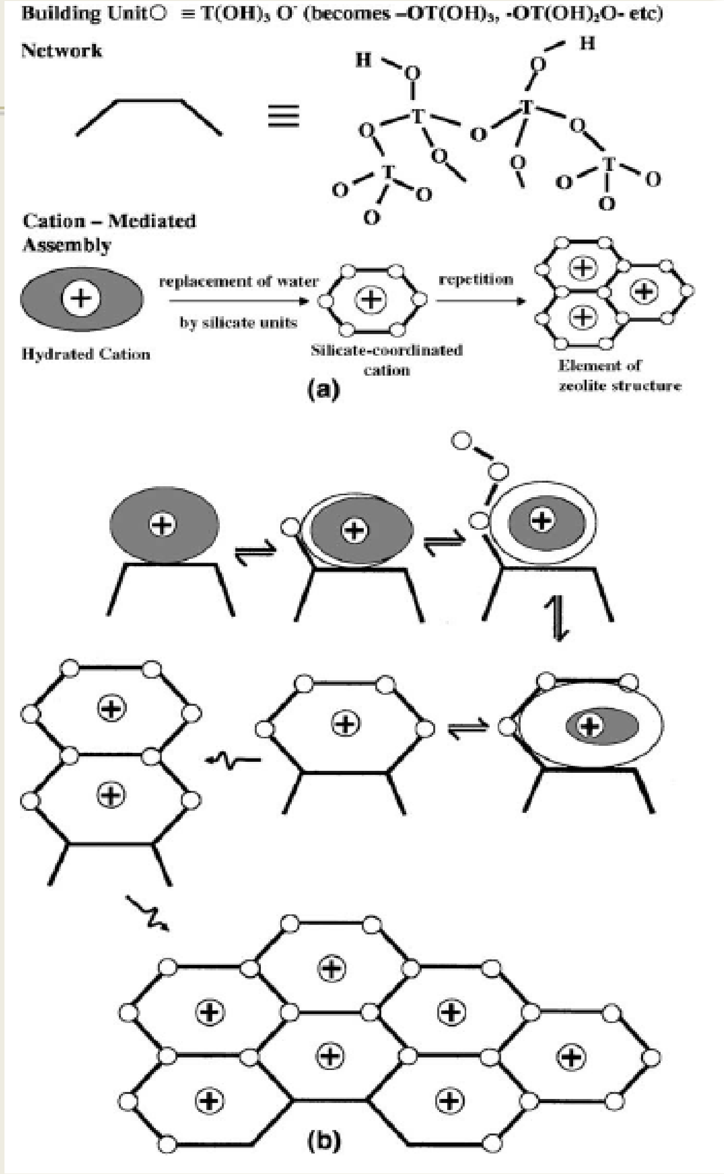


Fig. The basic mechanism for the cation-mediated assembly of ordered regions: (a) nomenclature and symbolism; (b) details of in-situ construction process by addition of solution units to a surface site

Ref : Phase transformation Textbook

Micropor. Mesopor. Mater. **2005**, 82, 1.

3.3. Synthesis of Zeolites

Crystal growth

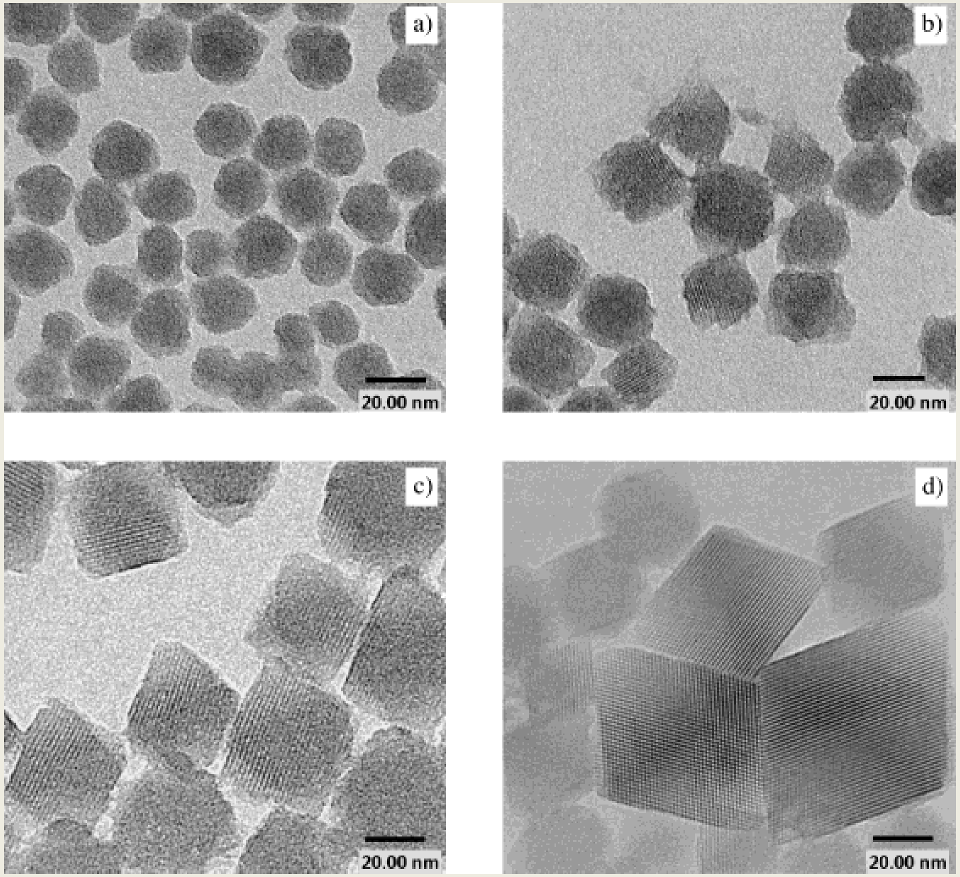


Fig. Particles in a) freshly prepared aluminosilicate solution for the synthesis of zeolite Y and after hydrothermal treatment at 100˚C for b) 28, c) 48, and d) 75 h

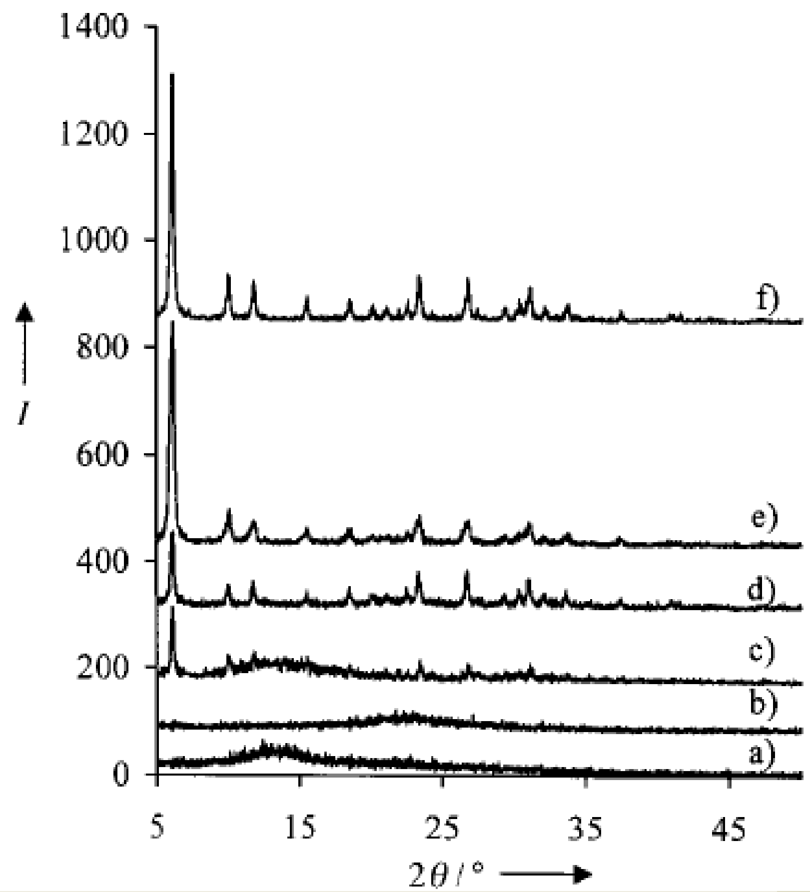


Fig. Powder diffraction patterns of a) the freshly prepared solution for the synthesis of zeolite Y (containing all reagents) and after hydrothermal treatment for b) 24, c) 28, d) 38, e) 55, and f) 75 h.

Angew. Chem. Int. Ed., **1999**, 38, 3201.

3.3. Synthesis of Zeolites

Crystal growth

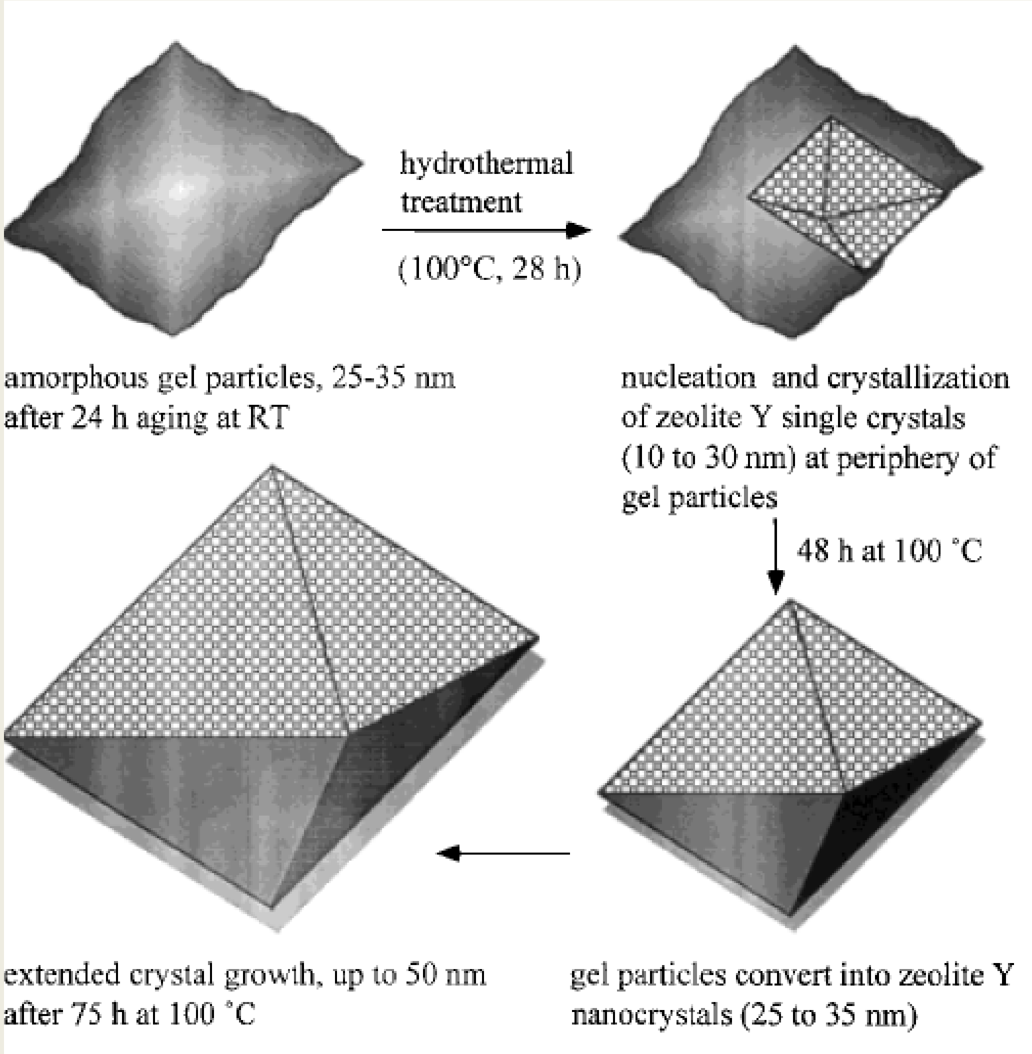


Fig. Proposed reaction scheme for the zeolite growth mechanism in colloidal solution.

Angew. Chem. Int. Ed., **1999**, 38, 3201.

3.3. Synthesis of Zeolites

Crystal growth (Detail)

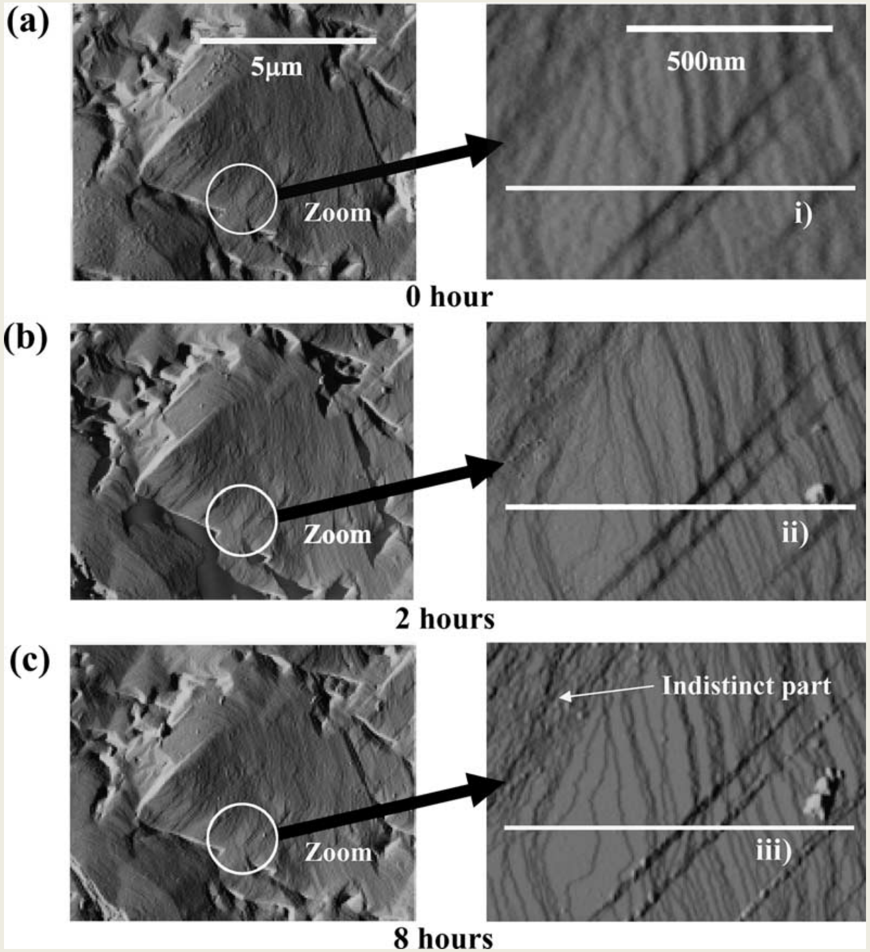


Fig. Changes in the faujasite surface at the same position on a (1 1 1) face during seeded growth observed by AFM. The images were taken at (a) 0 h, (b) 2 h, and (c) 8 h of the growth period

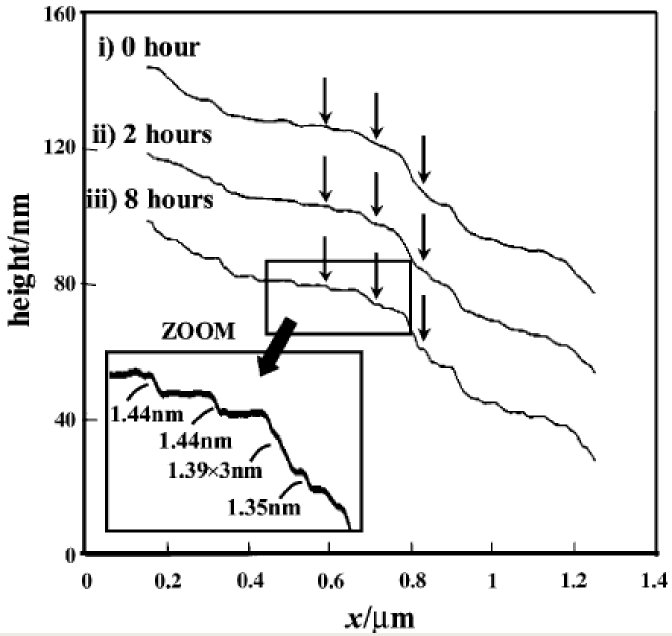


Fig. Cross-sectional profiles of (i), (ii) and (iii) along with the lines as labeled in (a), (b), and (c), respectively.

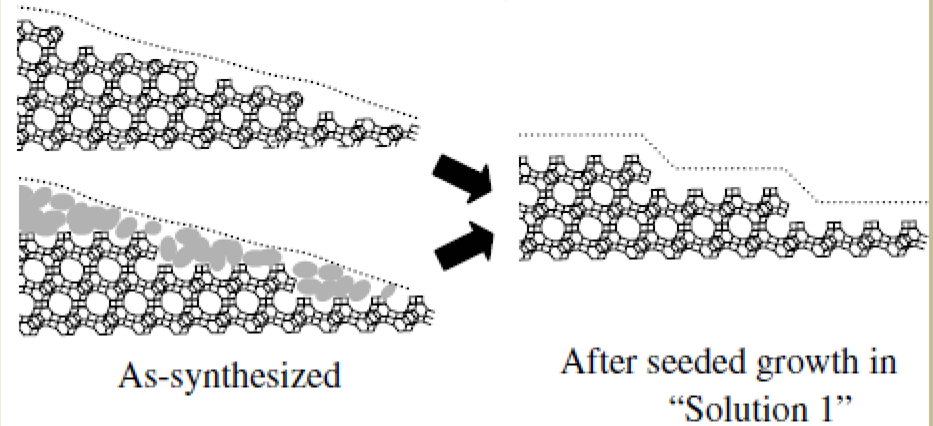
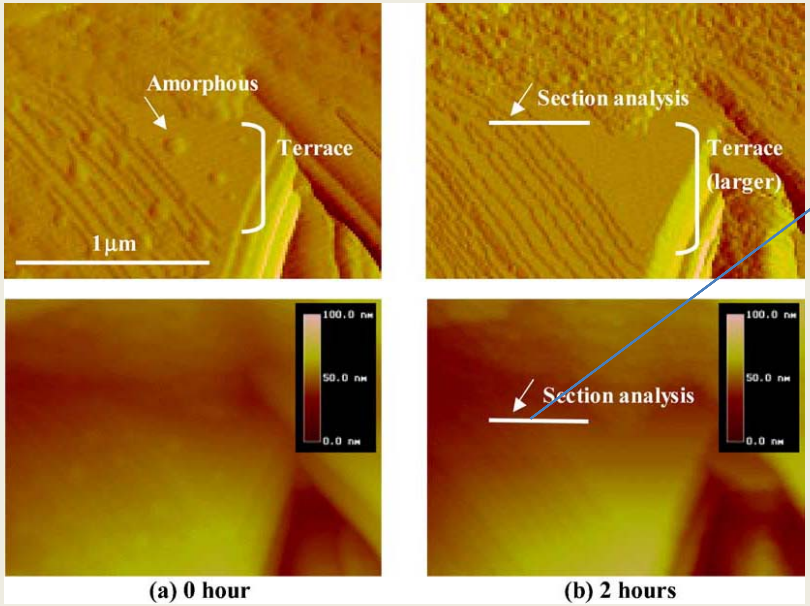


Fig. A model of the changes in the top-surface structure. The left part is a model of as-synthesized faujasite. The top surface is terminated with various structures (upper left) and/or is covered with amorphous matter (lower left). The right part is after the seeded growth in solution 1, where it is assumed that the top surface is terminated with D6Rs as shown in Fig. 5(c)

Micropor. Mesopor. Mater. **2004**, 70, 7.

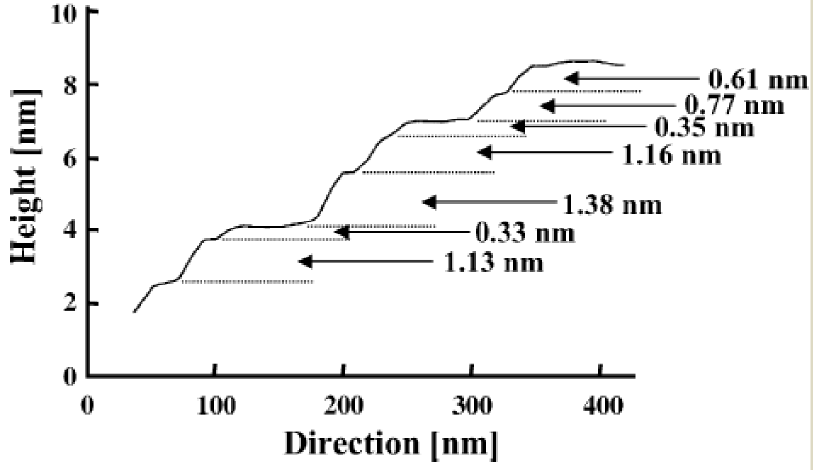
3.3. Synthesis of Zeolites

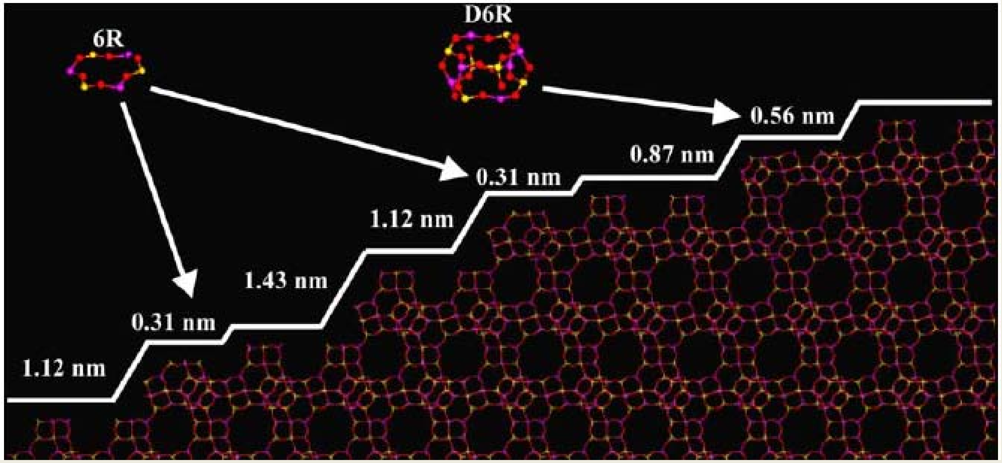
Crystal growth (Detail)



(a) 0 hour (b) 2 hours

Fig. Magnified images of the lower part of Fig. 8, as labeled (a) 0 h and (b) 2 h





✓ The rough surface of the seed changed into a well-ordered (1 1 1) face during the seeded growth near equilibrium.

✓ This surface ordering proceeded by thermodynamic stabilization of the top-surface structure via the mutual transfer of aluminosilicate species between the solution and solid phases, and/or by dissolution of the amorphous matter on the seed.

Micropor. Mesopor. Mater. **2004**, 70, 7.

3.4. Zeolite Template for Organic Nanomaterial Synthesis

Zeolite Templated Carbons (ZTC)

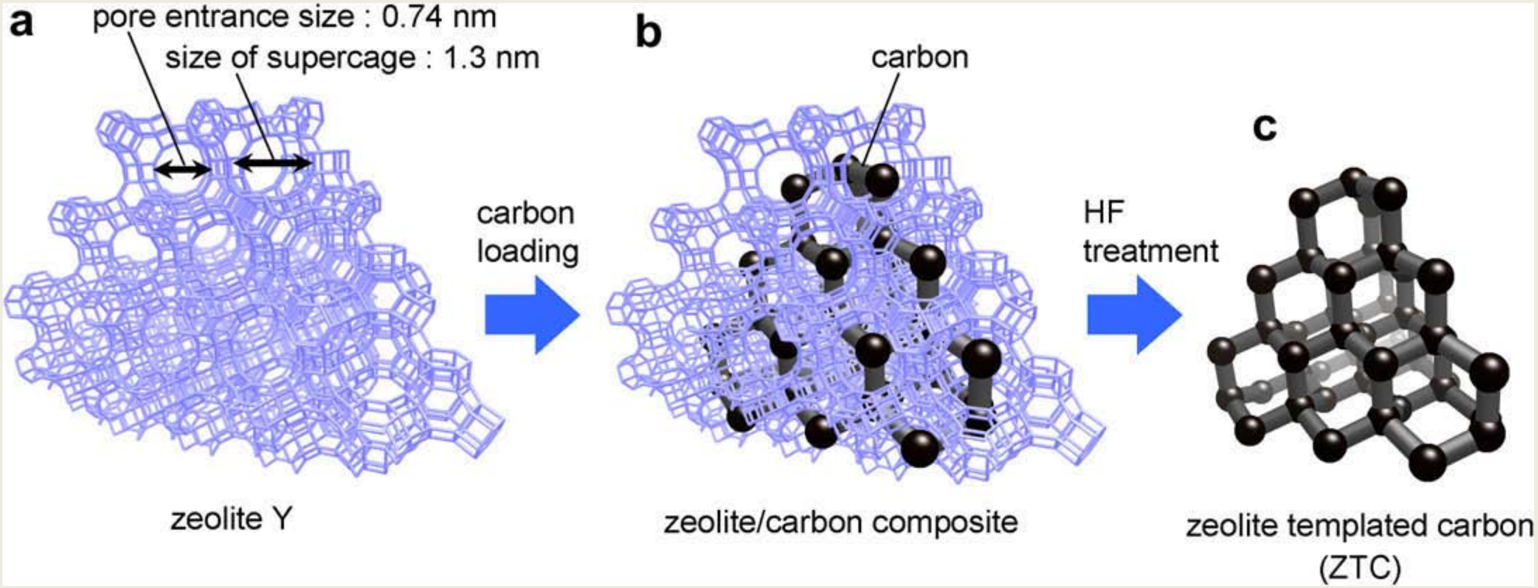


Fig. Synthesis procedure of the ZTC. (a) Crystal structure of the zeolite Y template, (b) illustration of zeolite/carbon composite. Impregnated carbon is shown by a black framework and (c) framework structure of the liberated ZTC after HF washing.

Carbon, **2009**, 47, 1220.

3.4. Zeolite Template for Organic Nanomaterial Synthesis

Zeolite Templated Carbons (ZTC)

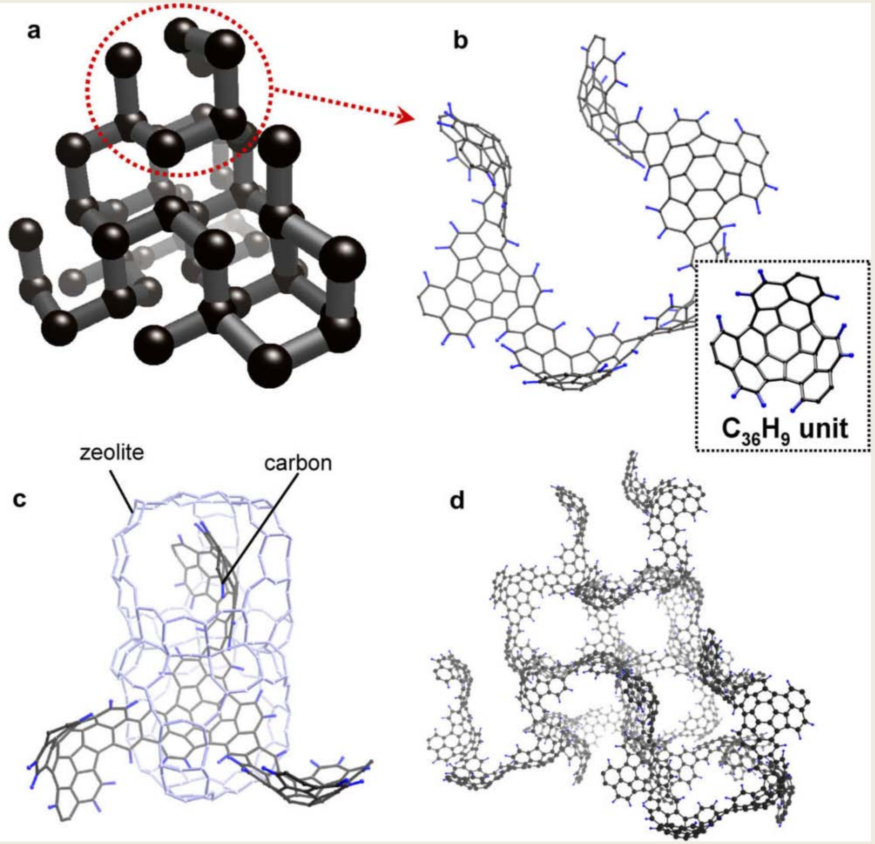


Fig. Idealized molecular model containing only carbon and hydrogen atoms. (a) A ball and stick model for the structure of the ZTC framework. Black sphere and gray stick correspond to a basic buckybowl unit and the connection between two units, respectively, (b) an idealized molecular model constructed with six buckybowl units of C36H9 (inset). All the graphene edges are passivated with hydrogen atoms. The structure in (b) corresponds to the part indicated by a dotted circle in the network structure in (a), (c) the molecular model constructed with four buckybowl units with zeolite framework and (d) a large-sized molecular model that is constructed with the buckybowl units following the regularity of the zeolite Y template. The model (d) has the same network structure as the model (a)

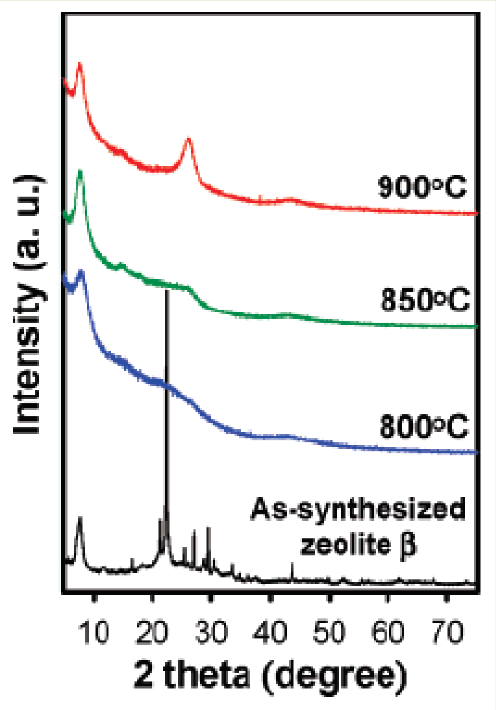
Carbon, **2009**, 47, 1220.

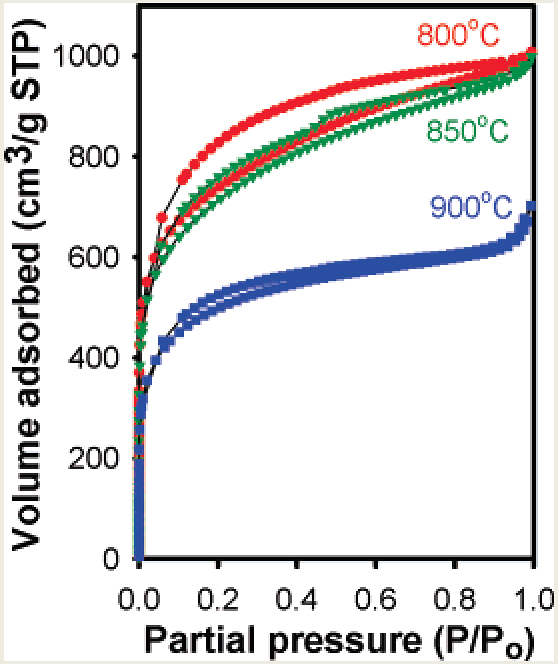
3.4. Zeolite Template for Organic Nanomaterial Synthesis

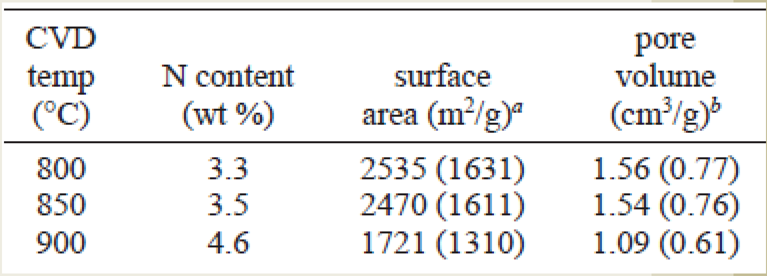
Zeolite-Like Carbons Nanocast Using As-Synthesized Zeolite Templates

Synthesis procedures:

1. An alumina boat with 0.5 g of dry as-synthesized zeolite β was placed in tube furnace
2. Heated to the required temperature (800-900 °C) under a flow of nitrogen saturated with acetonitrile for 3 h and cooling under a flow of nitrogen only.
3. Resulting zeolite/carbon composites were recovered and washed with 25% hydrofluoric (HF) acid for 3 days to remove the zeolite framework







CVD temp (°C)	N content (wt %)	surface area (m^2/g)^a	pore volume (cm^3/g)^b
800	3.3	2535 (1631)	1.56 (0.77)
850	3.5	2470 (1611)	1.54 (0.76)
900	4.6	1721 (1310)	1.09 (0.61)

J. Phys. Chem. C., **2008**, 112, 2764.

3.4. Zeolite Template for Organic Nanomaterial Synthesis

Zeolite-Like Carbons Nanocast Using As-Synthesized Zeolite Templates

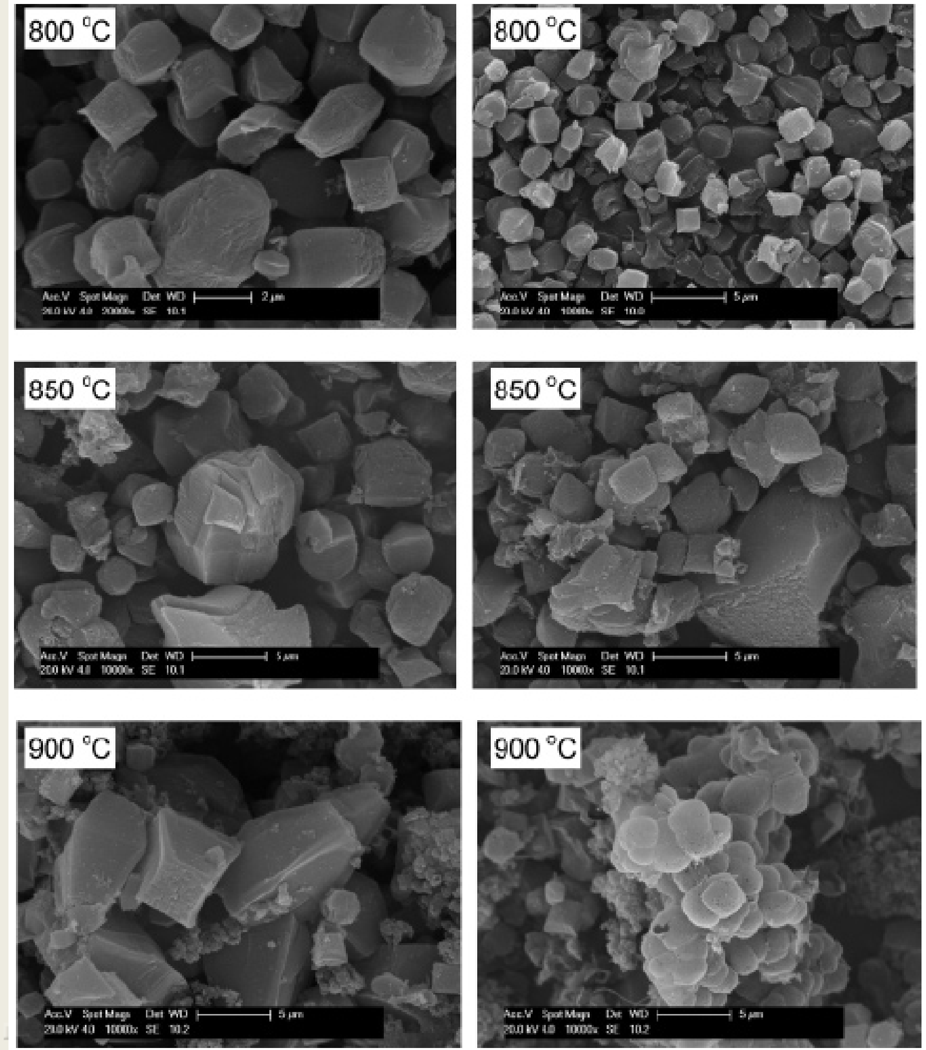


Fig. SEM micrographs of carbon materials prepared using zeolite template via CVD at various temperature

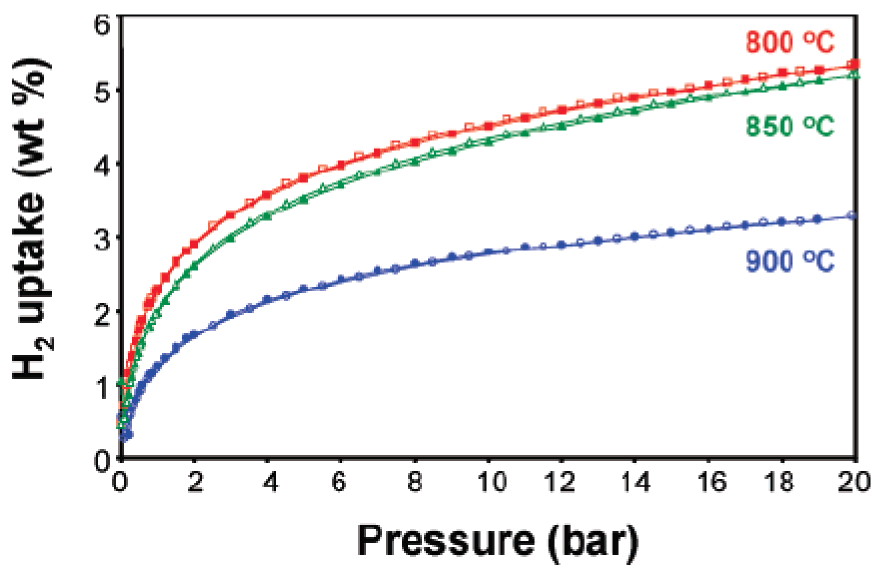


Fig. Hydrogen sorption isotherms at -196 °C of carbons obtained via CVD at various temperatures using as-synthesized zeolite as template.

J. Phys. Chem. C., **2008**, 112, 2764.