CH5716
Processing of Materials

Prof. J.T.S. Irvine

Lecture JI2 – Sol gel + intercalation

Sol gel processing

Two approaches

1) Dispersion of colloidal particles (often oxides) in a liquid to give a solution, which upon manipulation of pH or concentration undergoes gelation.

2) Preparation of a metal-organic precursor in solution, which upon addition of H_2O, undergoes gelation.

Features

- low temperature synthesis (small particle size, homogeneous on atomic scale)
- synthesis of new phases possible
- capacity to form films and fibres
- high cost
- long processing time - complex

Uniform solution $\xrightarrow{\text{Controlled hydrolysis \& nucleation}}$ **Sol** $\xrightarrow{\text{Hydrolysis \& Gelation}}$ **Gel**

Gel $\xrightarrow{\text{Hypercritical drying}}$ **Aerogel**

Gel $\xrightarrow{\text{Solvent evaporation}}$ **Xerogel**

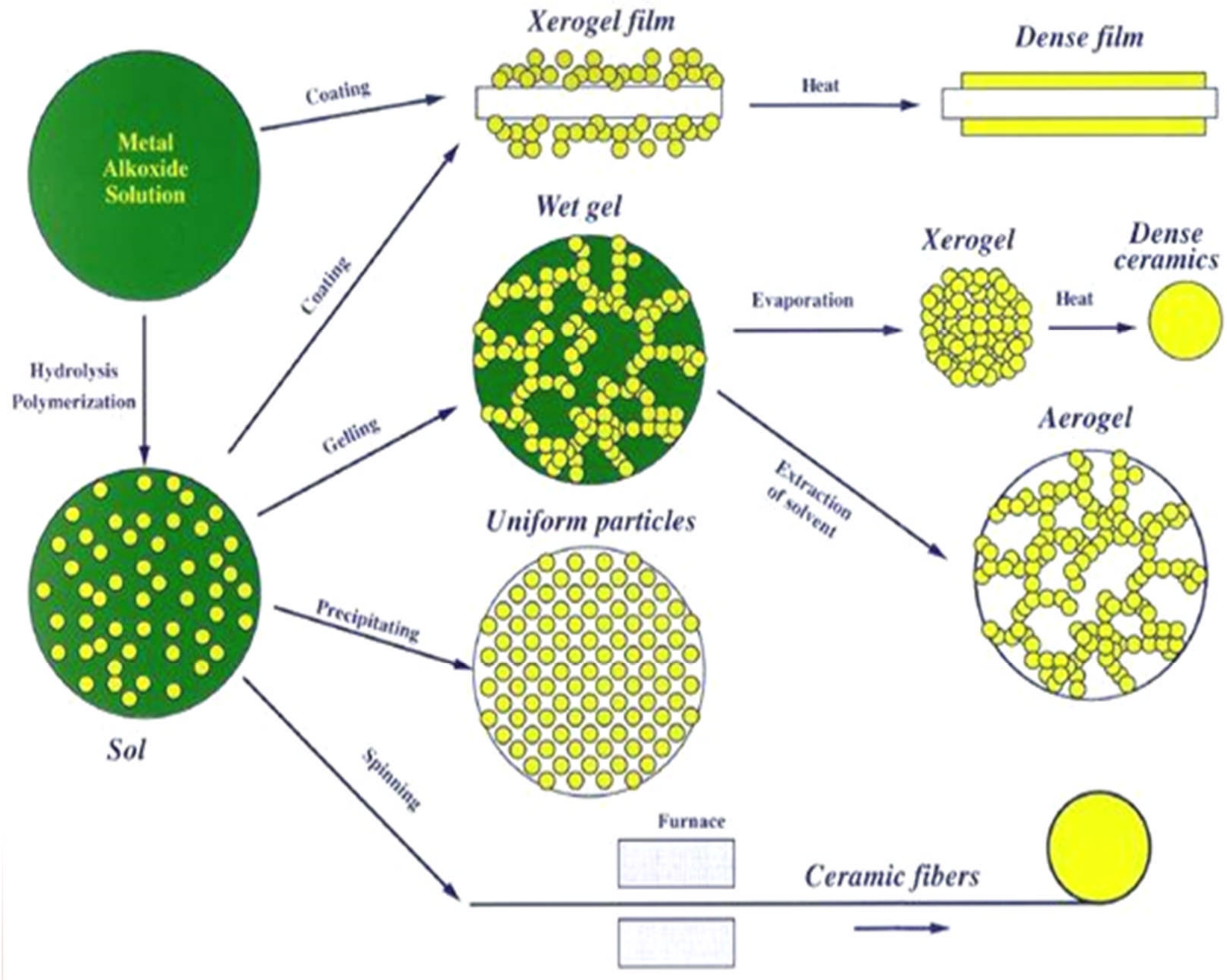
Aerogel → **Monoliths**

Xerogel $\xrightarrow{\text{Heat grind and press}}$ **Dense Ceramic**

Xerogel $\xrightarrow{\text{Heat}}$ **Dense film**

A classic silica aerogel monolith
(image credit Prof. C. Jeffrey Brinker)
http://www.aerogel.org/?p=3

Aerogels - formed with minimal shrinkage, cracking
- 1% of volume solid
- high strength-mass ratios


Metal Alkoxide Solution
Coating
Xerogel film
Heat
Dense film
Hydrolysis
Polymerization
Coating
Wet gel
Evaporation
Xerogel
Heat
Dense ceramics
Gelling
Aerogel
Extraction of solvent
Uniform particles
Precipitating
Sol
Spinning
Furnace
Ceramic fibers

Non-aqueous routes

For alkoxide route

Hydrolysis

$$M(OR)_x + x\,H_2O \rightarrow M(OH)_x + x\,ROH$$

Condensation

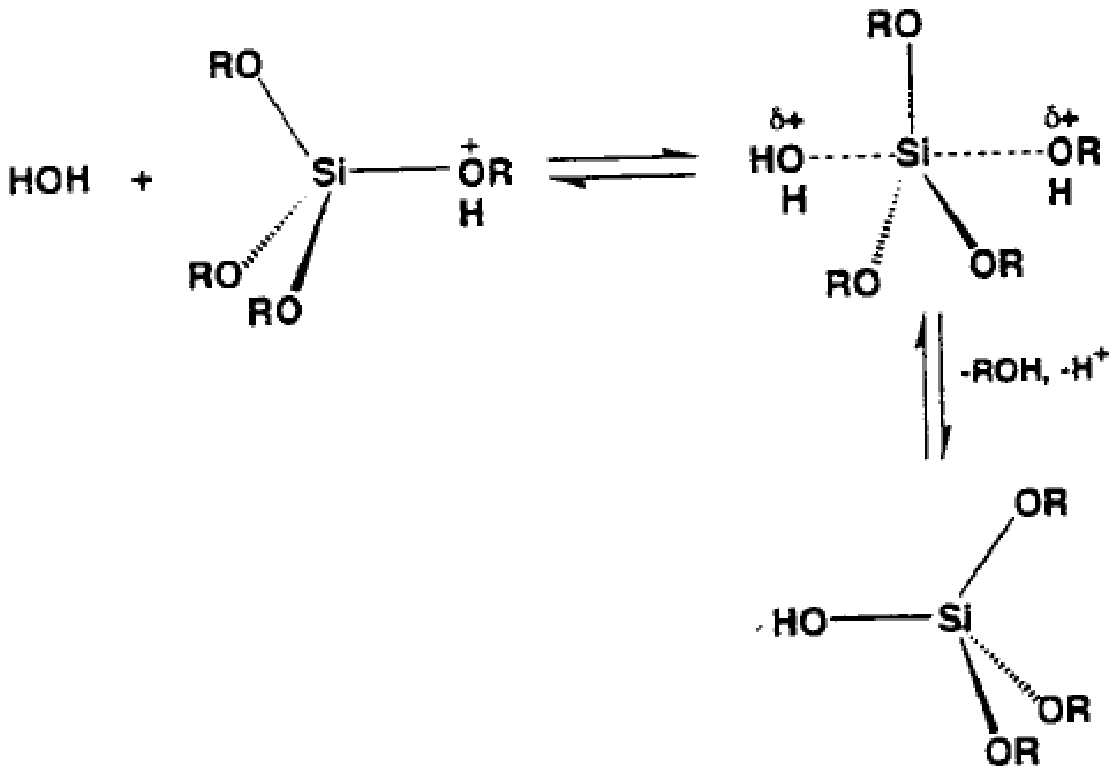
$$2M(OH)_x \rightarrow (HO)_{x-1}MOM(OH)_{x-1} + H_2O$$

Hydrolysis/condensation reactions lead to dimers-polymers-gels

Sol gel Mechanisms - for Si alkoxides **Initial Step Hydrolysis**

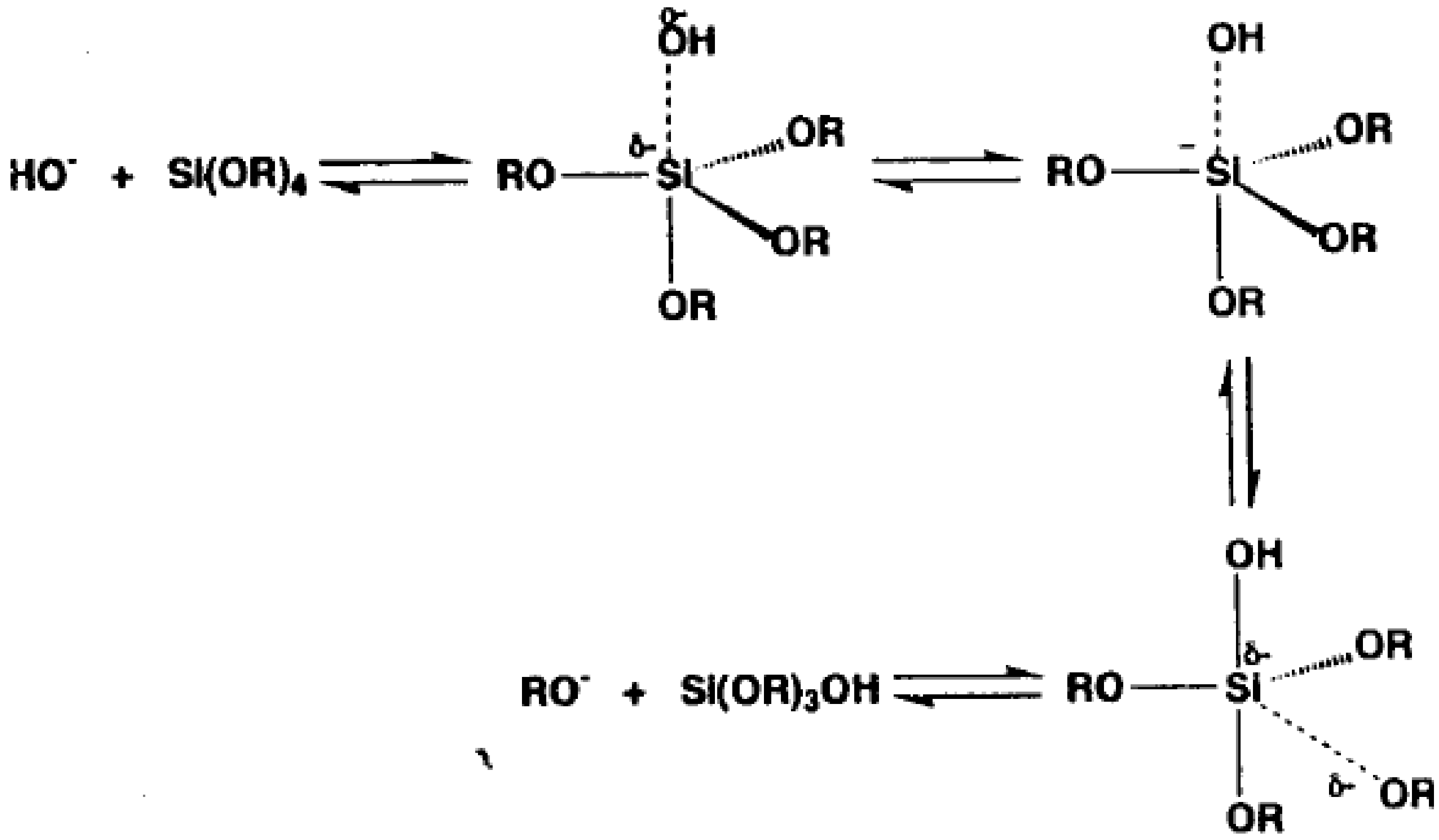
Low water/ Acid catalysis

Hydrolysis S_N2 nucleophillic substitution



Acids enhance kinetics - produce good leaving groups and eliminate requirement for proton transfer in transition state.
Acid catalysed directed towards ends - linear chains

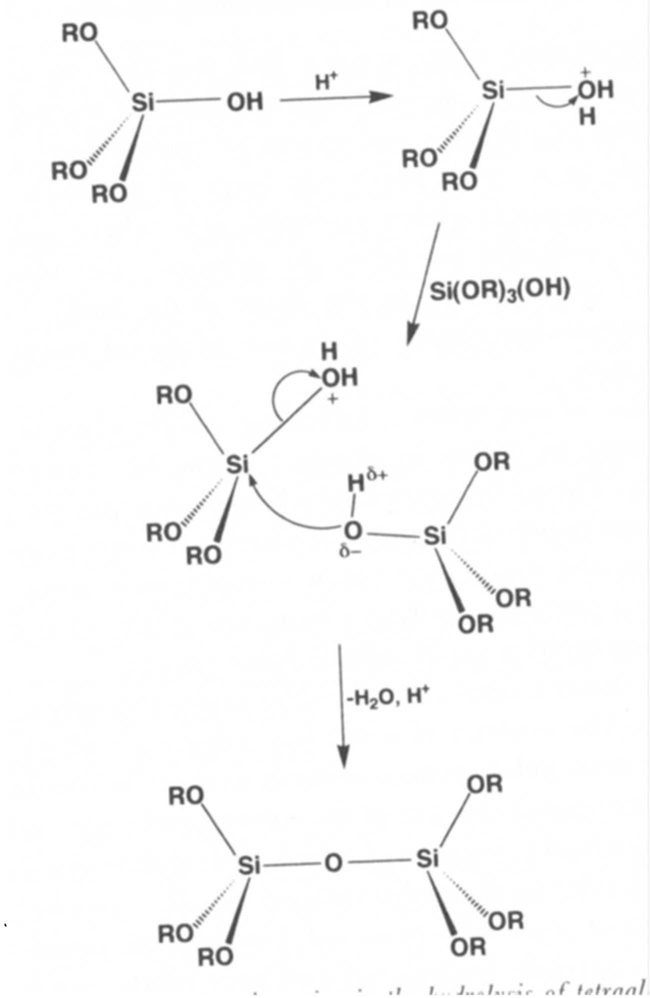
High Water/Base catalysed



Base catalysed leads to highly branched polymers

Condensation

via nucleophilic condensation
mechanism water release
generally favoured

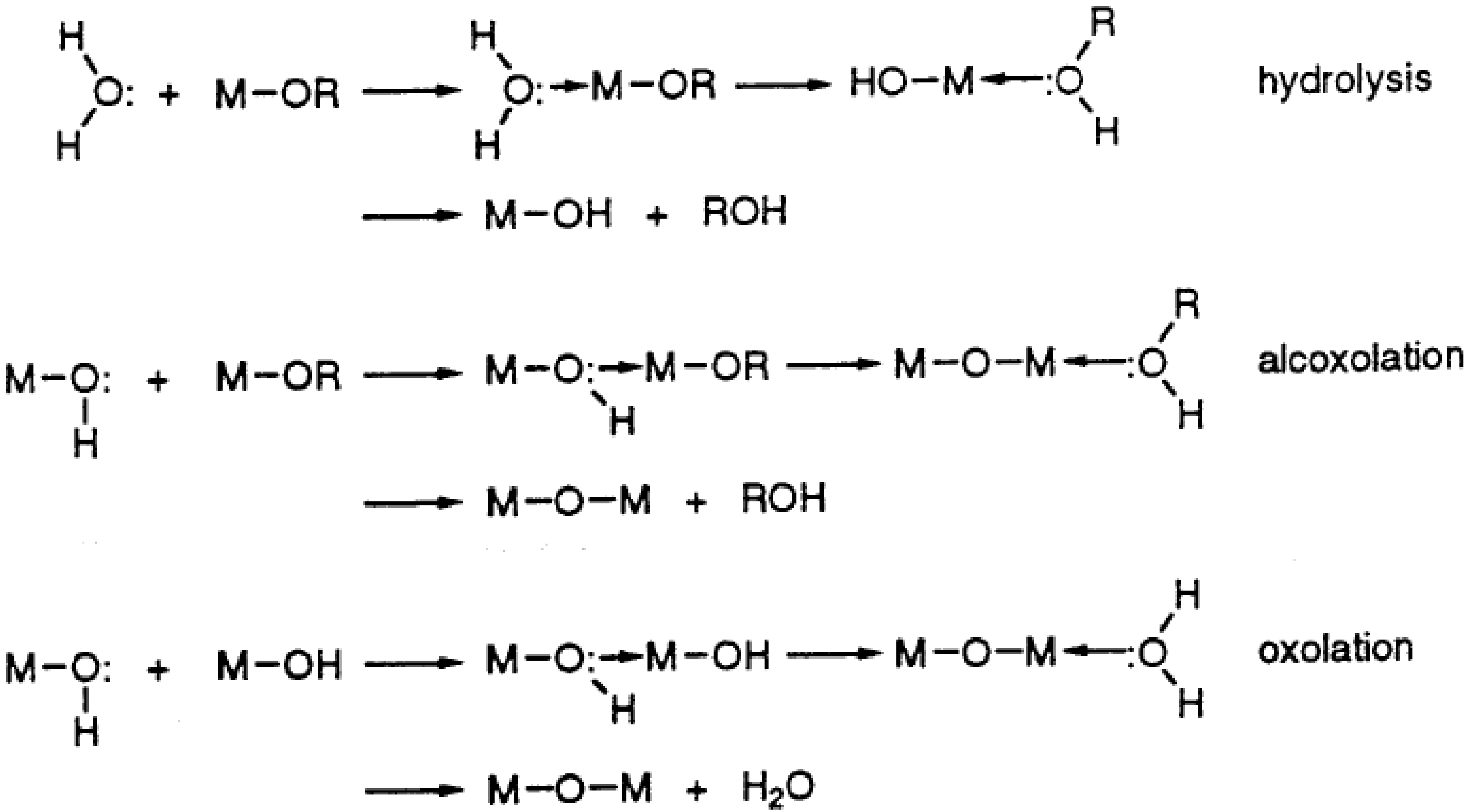


Hydrolysis and condensation occur

Nature of final product depends upon
pH, water/alkoxide ratio (*r*)

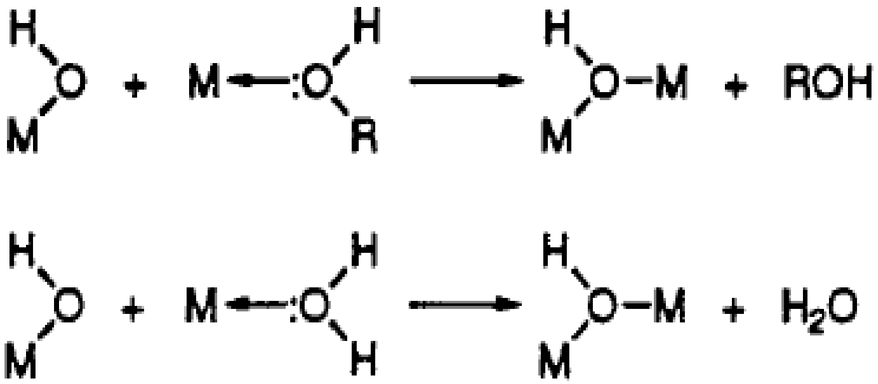
Ti, Zr alkoxides d^0

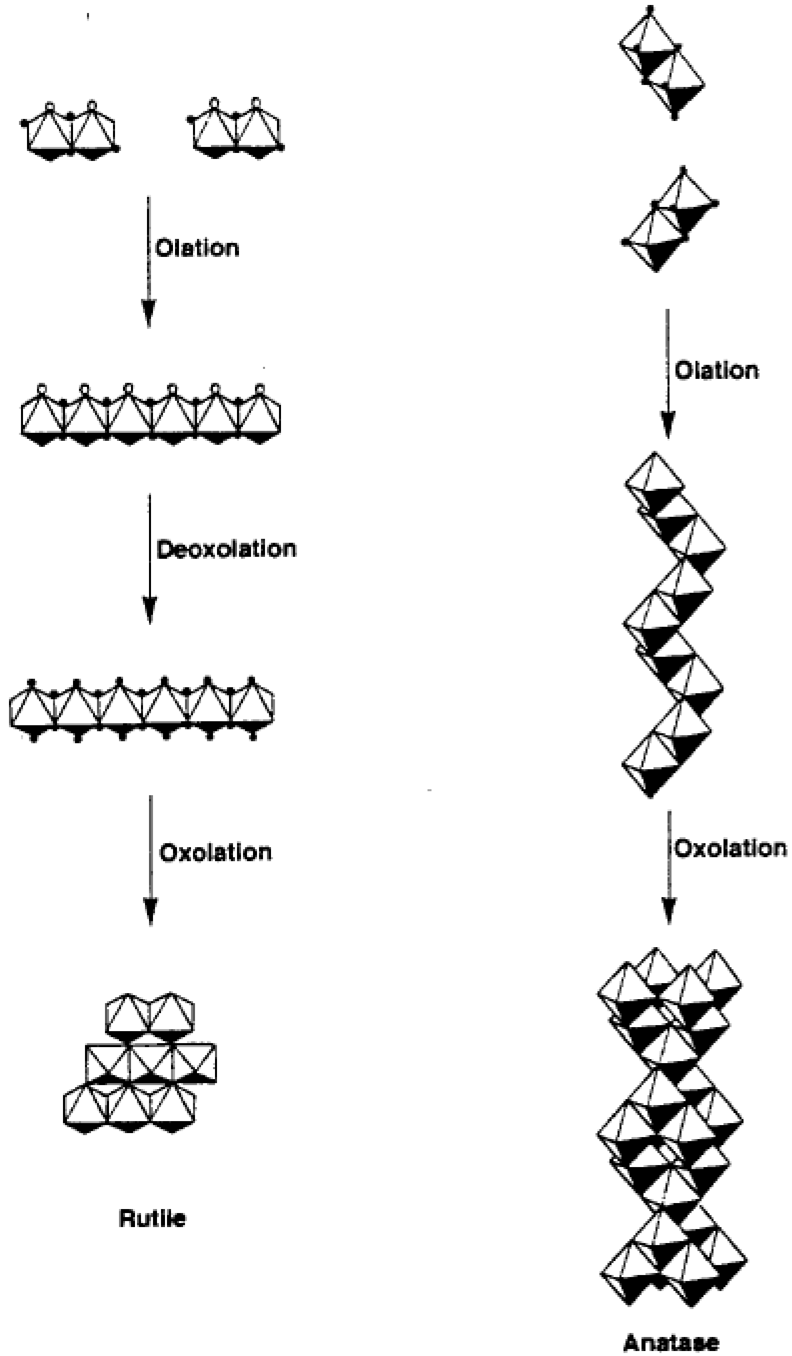
hydrolysis rates and condensation rates for Ti alkoxides @10^4 times higher than for silicon alkoxides



Condensation Pathways for TiO_2

Olation





Non-hydrolytic sol-gel processing

Conventional sol-gel: formation of M-O-M bridges through hydrolysis and condensation reactions

Si alkoxides, transition metal alkoxides vastly different hydrolysis rates

Alternative route: M-O-M bridges obtained by condensation between halide and alkoxide with elimination of alkyl halide

$$\text{M-X} + \text{M-OR} \rightarrow \text{M-O-M} + \text{R-X}$$

e.g. SiO_2/TiO_2, SiO_2/ZrO_2 solid solutions

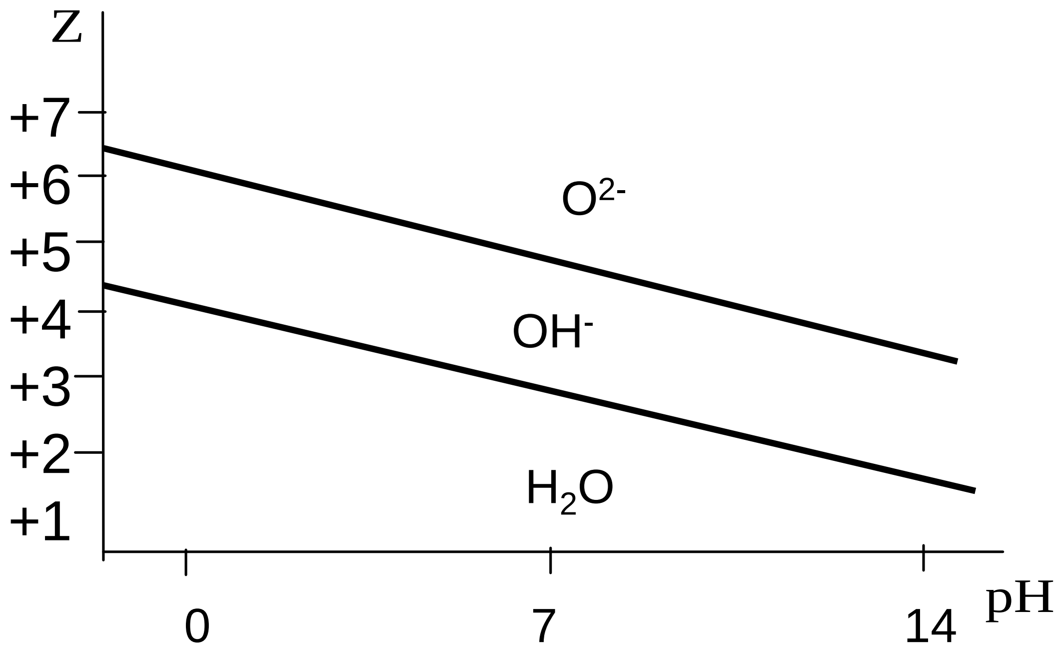
Aqueous routes

Sol Gel and Aqueous Chemistry of Metal Oxides

more complex than alkoxide owing to the occurrence of spontaneous hydrolysis and condensation reactions in the aqueous medium, dependent on pH, concentration, temperature

hydrolysis

$$[M(OH_2)_N]^{Z+} + hH_2O \rightarrow [M(OH)_h(OH_2)_{N-h}]^{(Z-h+)} + hH_3O^+$$



hydrolysis continues until mean electronegativity of hydrolysed precursor χ_p equals that of the aqueous solution χ_w

χ_w = 2.732- 0.035 pH

h depends on Z and pH

Condensation occurs on going into the hydroxo regime from either the aquo- or the oxo- regimes

pH for condensation can be predicted.

Condensation of Inorganic sol-gel systems

Aquo/hydroxo regime - 2 mechanisms

Olation - ol bridges

$$M\text{-}OH + M\text{-}OH_2 \longrightarrow M\text{-}OH\text{-}M + H_2O$$

only occurs where aquo-precursors have their maximum coordination number

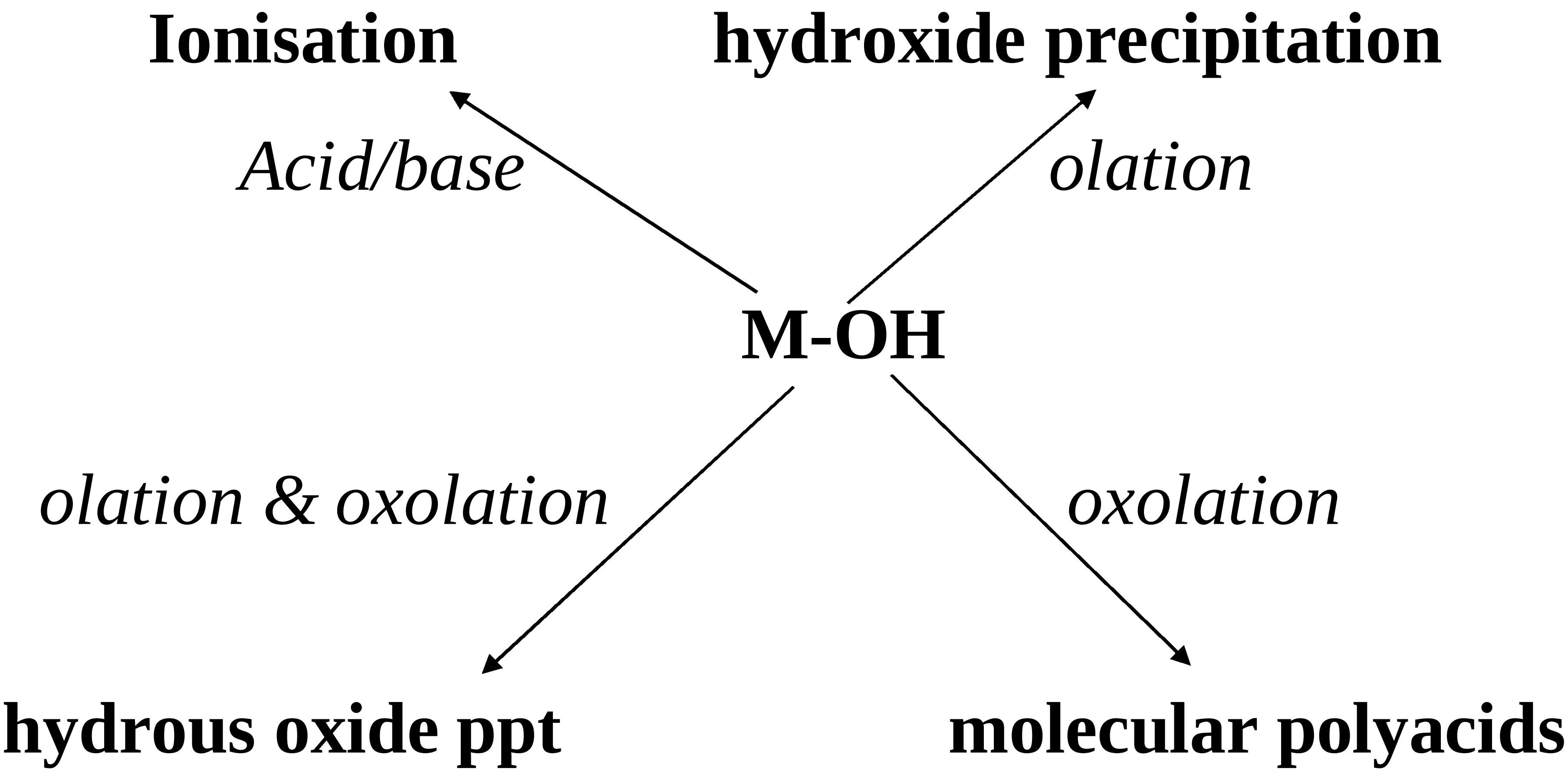
Oxolation

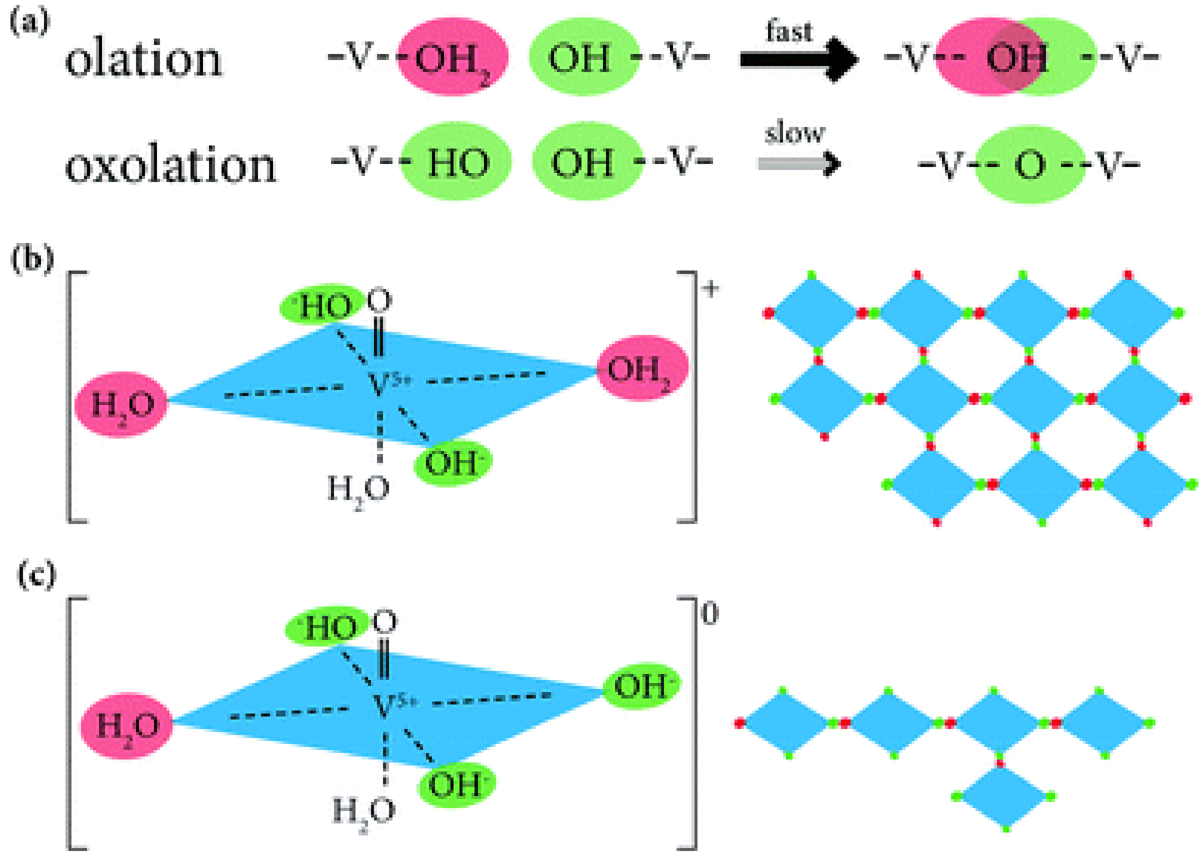
Nucleophilic addition of OH groups onto metal ions is followed by 1,3 proton transfer to form an oxo bridge

$M{-}OH\cdots M{-}OH$ *transition state*

$M{-}O{-}M{-}OH_2$

Chemistry depends upon electronegativity of cation


Ionisation
hydroxide precipitation
Acid/base
olation
M-OH
olation & oxolation
oxolation
hydrous oxide ppt
molecular polyacids



Schematic sketch of precursor condensation forming low-dimensional $NH_4V_3O_8$ networks. The simplified olation and oxolation processes are shown in (a). Considering predominant fast olation reactions, positively charged (b) and neutral (c) precursors yield the formation of 2D and 1D networks, respectively.

Zakkarova et al DOI: 10.1039/C3DT32550D Dalton Trans., 2013, **42**, 4897-4902

High valent cations ($z>4$)

oxohydroxo anions $[MO_x(OH)_{m-x}]^{(m+x-z)-}$ in aqueous solution

condensation only possible by oxolation (as no H_2O molecules coordinated to metal)

Two mechanisms

1. If coordination expansion of metal is possible: nucleophilic addition via M-OH or M=O. Chains and rings are formed very rapidly $\rightarrow$ edge or face sharing polyhedra

2. If no coordination expansion is possible: nucleophilic substitution $\rightarrow$ corner sharing polyhedra
$M\text{-}OH + M\text{-}OH \rightarrow M\text{-}O\text{-}M\text{-}OH_2$

Alternative possibilities

TiO_2

1. Na_2TiO_3 in conc HCl + base ->TiO_2 gel

TiO_2: anatase or rutile depending upon conditions eg pH

2. $Ti(OR)_4$ R = Et, n-Pr, i Pr, n-Bu etc

Dissolve in ROH, add H_2O in alcohol, with HCl/HNO_3 catalyst

Sintering and grinding of gel results in ultrafine TiO_2 powder with high surface area

-catalysis, photocatalysis, ceramic products

$BaTiO_3$

Ferroelectric material used in capacitors, thermal cut-out switches etc.

1. $Ti(OR)_4$ + hydrated salt of barium in ROH -> gel

2. $Ba(OEt)_2$ + $Ti(OEt)_4$ -> gel

3. BaTi complex organometallic precursors eg Ba_4Ti_{13} nucleus

1000^oC sufficient to produce 90% dense ceramic
1300-1500 normally required for $BaTiO_3$

Biomineralisation

Biology is a master of chimie douce.

Consider calcite - $CaCO_3$

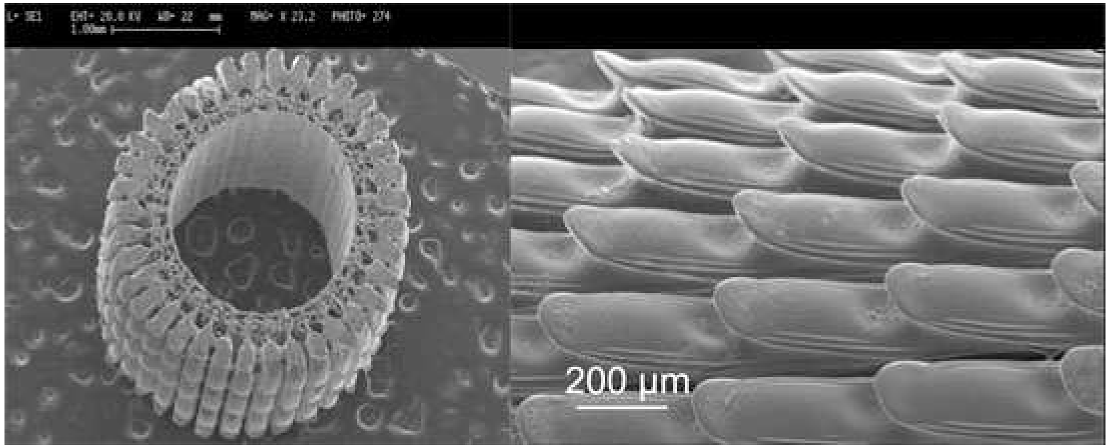
lab samples grown at room temperature cubic
20μ edge best examples

Sea urchin spines also single crystals, 2mm

contain 0.02wt% protein

1 molecule - 10^5 unit cells

Biomineralisation



Sea urchin spines also single crystals, 2mm

contain 0.02wt% protein

1 molecule - 10^5 unit cells

http://www.asianscientist.com/in-the-lab/sea-urchins-spiny-strength-calcite-crystals-2012/

INTERCALATION

MX_n phases with layered or tunnel structures can be intercalated at room temperature with lithium to give reduced phases A_xMX_n

(i) Topochemical, little rearrangement of host
(ii) reversible reaction, chemical or electrochemical
(iii) Cations and electrons transferred - *mixed ionic/electronic conductors.*

Insertion - similar process but into a 3-d host lattice

Chemical -

$$x\ BuLi + TiS_2 \longrightarrow Li_xTiS_2 + x/2\ C_8H_{18}$$

Electrochemical

e^-

$\longrightarrow$

Li^+

$\longrightarrow$

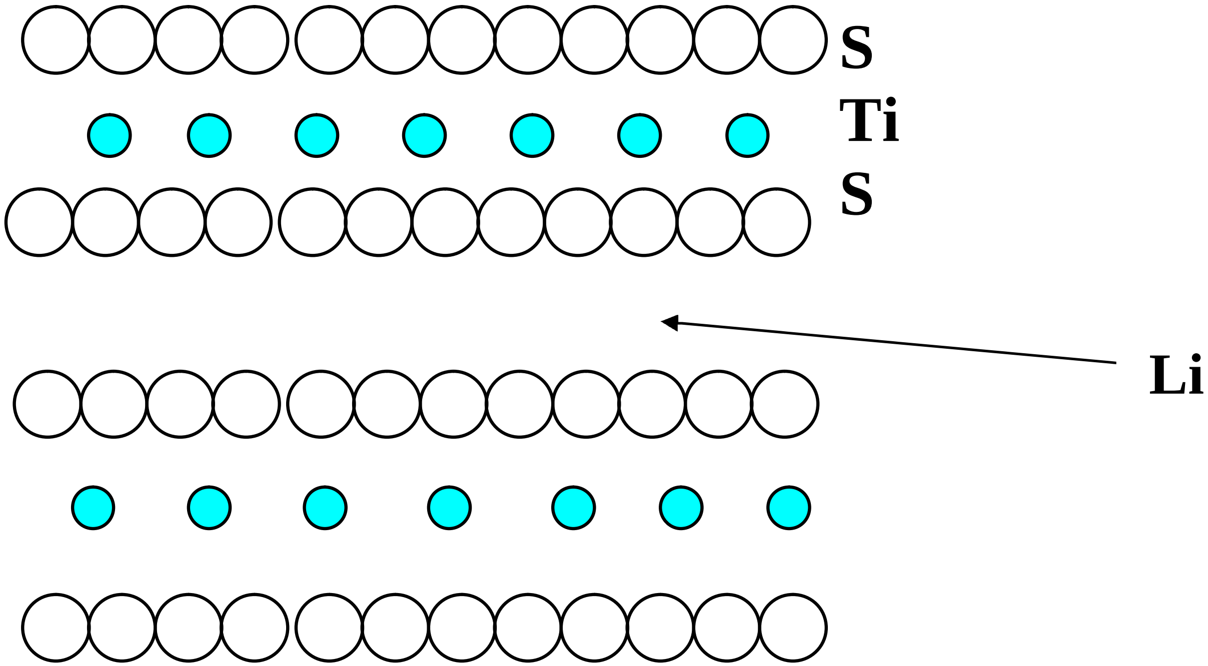
Li/Al | $LiClO_4$/ CH_3CN | Li_xTiS_2

$$Li \longrightarrow Li^+ + e^-$$

$$Li^+ + TiS_2 + e^- \longrightarrow LiTiS_2$$

Mechanism

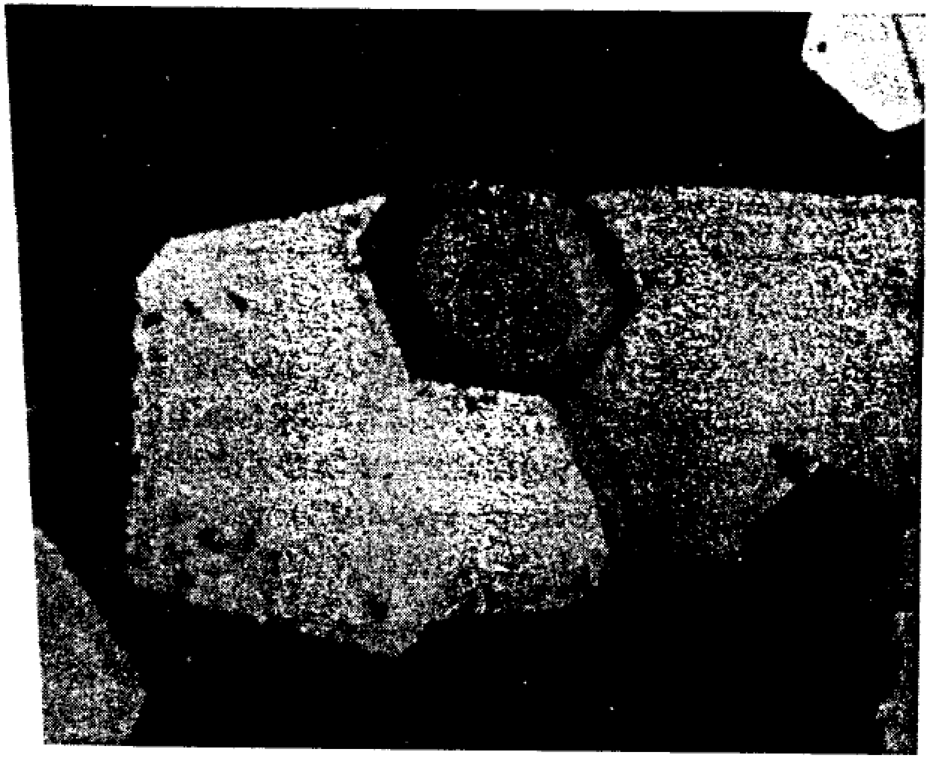
TiS_2 hcp S with Ti occupying 1/2 the octahedral interstices

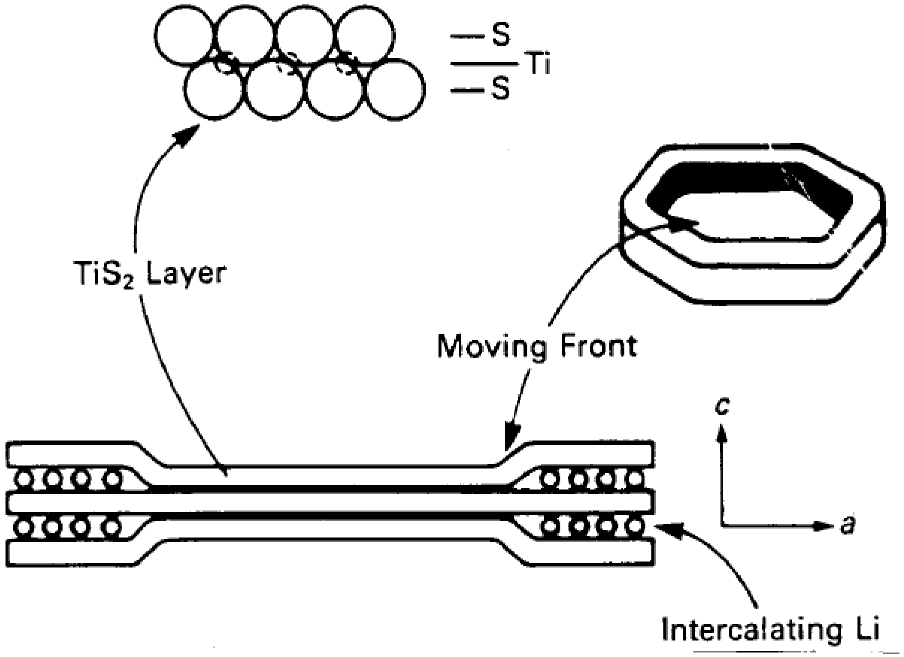


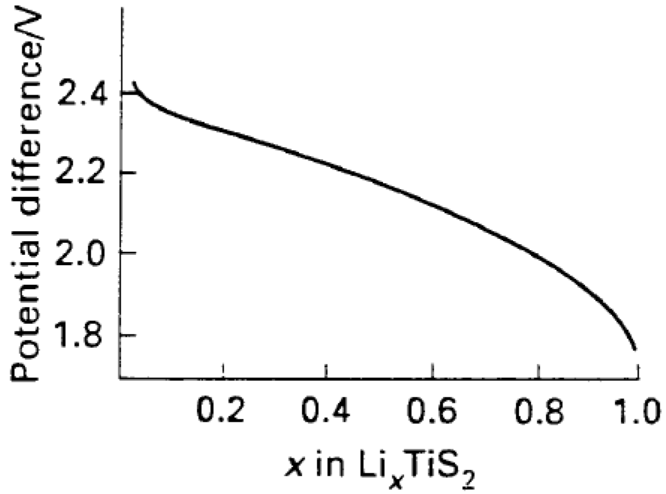
Li_xTiS_2 exists for $0 \leq x \leq 1$, no major change in structure, except for expansion in **c**.

Mechanism

For Li_xTiS_2 intercalation front starts at edge of crystal







Further Examples

$$\textbf{Graphite} + K \longrightarrow C_8K$$

$$\text{Graphite} + Na \longrightarrow C_8Na \quad \text{(superconductor)}$$

$$\mathbf{C_{60}} + Cs \longrightarrow Cs_3C_{60}$$

$$\textbf{Graphite} \xrightarrow{F_2/HF} C_4F$$

TiO_2, anatase

$$BuLi + 2TiO_2 \longrightarrow 2\ Li_{0.5}TiO_2 \text{ (anatase)}$$

$$2Li_{0.5}TiO_2 \xrightarrow{770K} LiTi_2O_4 \text{ (spinel,LT)}$$

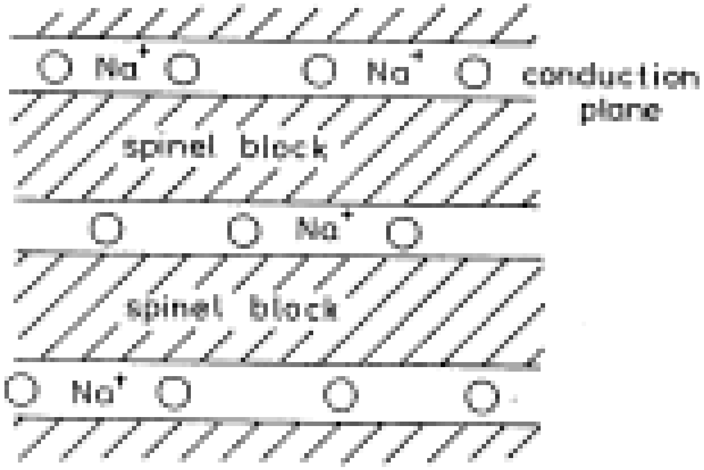
Chimie Douce - Ion Exchange

Intercalation + deintercalation

Oxide containing mobile ions

Heat in molten salt flux

Good example is Na^+ B alumina (@ $Na_2Al_{16}O_{25}$)

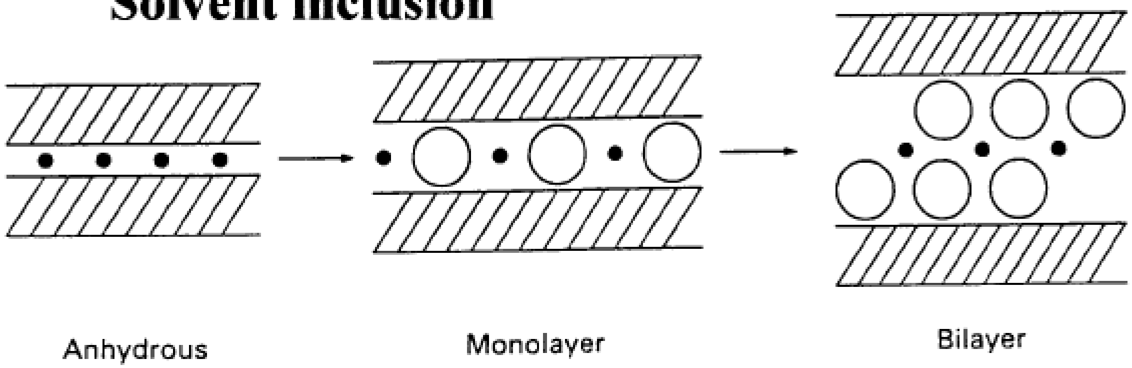


Na can be exchanged with

M^+ Li, K,Rb, Ag, Cu, NH_4, H_3O
M^{2+} Ca, Sr, Ba, Fe,
M^{3+} Eu, Nd, Fe

INTERCALATION OF NEUTRAL SPECIES

Solvent inclusion

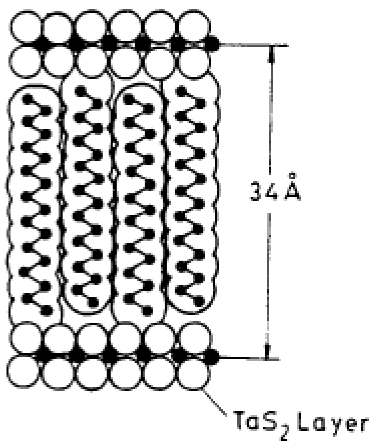


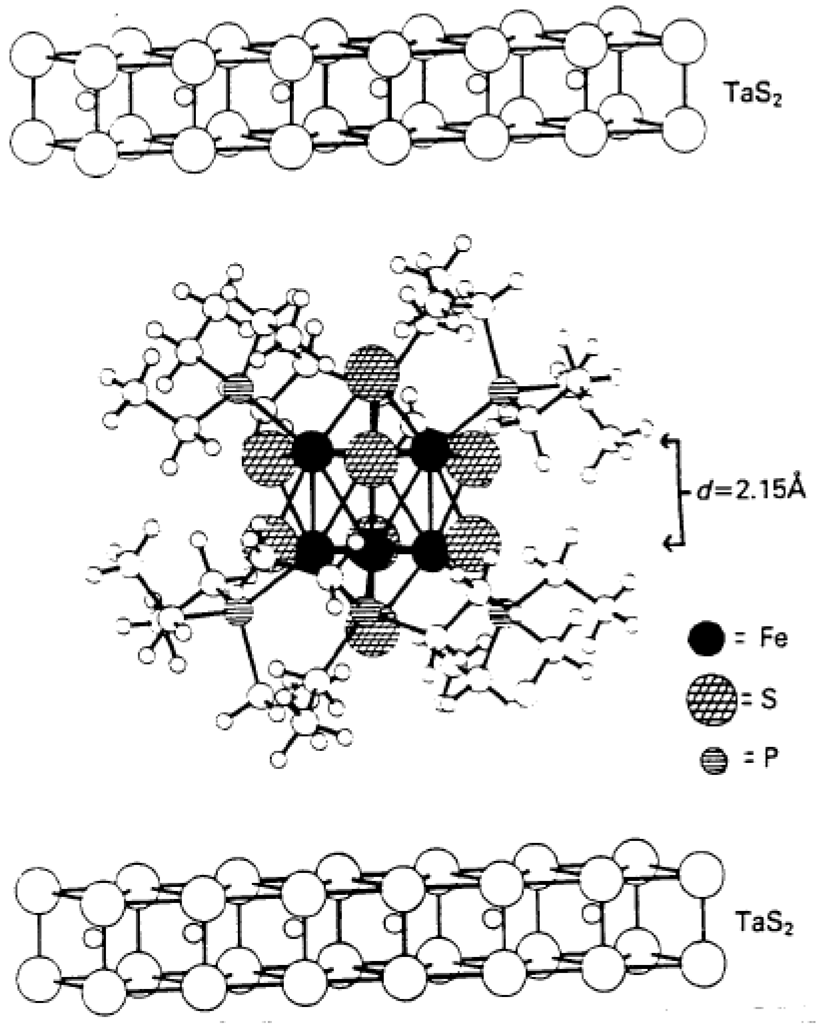
Na^+TaS_2

Solvent	Interlayer spacing Å
H_2O	11.9
EtOH	10.0
$HCONH_2$	16.4
$MeCONH_2$	18.9

Other species that can be intercalated

NH_3
pyridine
cobaltocene
chromocene
$[Fe_6S_8(P(C_2H_5)_3)_6]^{2+}$





Texts

SS reaction +
West Solid State Chemistry and its Applications

Sol Gel
David Thompson, Insights into Speciality Inorganic Chemicals

http://www.solgel.com/educational/educational.htm