ELSEVIER

Catalysis Today 41 (1998) 3–19

CATALYSIS TODAY

Sol–gel synthesis of heterogeneous catalysts from aqueous solutions

J. Livage*

Chimie de la Matière Condensée, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, France

Abstract

The formation of solid compounds from aqueous solutions is based on the hydrolysis and condensation of metal cations. When dissolved in water, metal salts give rise to solvated species in which the metal cation is surrounded by H_2O, OH^- or O^{2-} ligands. Condensation via olation or oxolation occurs in the pH range where OH ligands are present. Olation with low-valent cations rather leads to polycations and the precipitation of hydroxides whereas the oxolation of high-valent cations leads to the formation of polyanions and oxides. Complexation can also occur in the presence of foreign ions, allowing some chemical control of condensation reactions. These reactions will be described in the frame of the partial charge model. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Sol-gel; Hydrolysis; Condensation; Complexation

1. Introduction

Heterogeneous catalysts are often prepared by wet chemistry methods such as precipitation, coprecipitation, hydrothermal synthesis or sol–gel process. The main advantages of these low temperature processes are to give solids with large specific surface area and high porosity in the meso and macropore ranges. The solid network is formed, from the solution, via the hydrolysis and condensation of molecular precursors in solution. Two routes are usually defined, depending on the chemical nature of the precursors. The aqueous route is based on inorganic salts dissolved in water whereas alkoxides dissolved in organic solvents are used in the metal-organic route [1]. Only the aqueous route will be described here. This is actually the most widespread way of making heterogeneous catalysts. It is specially suitable for industrial applications [2]. A lot of research work is being done now on alkoxide sol–gel chemistry, but these precursors are much more expensive and difficult to handle than aqueous solutions [3].

2. Metal cations in aqueous solutions

2.1. Dissolution of metal salts in water

The molecular structure of the water molecule is characterized by two main features:

1. The oxygen atom being more electronegative than hydrogen (χ_O=3.5, χ_H=2.1) electron density in the H_2O molecule is shifted toward oxygen that bears a high negative charge. According to the partial charge model described at the end of this paper, this charge can be estimated as $\delta_O=-0.4$. As a consequence, the water molecule exhibits a

---

*Corresponding author. Tel.: 33 1 44 273365; fax: 33 1 44 274769.

PII S0920-5861(98)00034-0

high dipolar moment (μ=1.84 Debye) and liquid water has a high dielectric constant (ϵ~80). When dissolved in water, metal salts MX_Z are therefore dissociated into M^{Z+} and X^- ions which are then solvated by dipolar water molecules leading to the formation of $[M(OH_2)_N]^{Z+}$ species.

However water is also a Lewis base and the formation of $M–OH_2$ bonds with the metal cation (Lewis acid) draws electrons away from the bonding $\sigma(3a_1)$ molecular orbital of the water molecule toward the empty orbitals of the metal ion. This electron transfer weakens O–H bonds and coordinated water molecules behave as stronger acids than solvent water molecules. Aquo-cations behave as Brønsted acids and spontaneous deprotonation may take place as follows:

$$[M(OH_2)_N]^{Z+} + hH_2O \Leftrightarrow [M(OH)_h(OH_2)_{N-h}]^{(z-h)+} + hH_3O^+, \quad (1)$$

where h can be defined as the hydrolysis ratio. It corresponds to the number of protons that have been removed from the solvation sphere of the aquo-cation.

$$M^{Z+} - OH_2 \Leftrightarrow M^{Z+} - OH^- + H^+ \Leftrightarrow M^{Z+} - O^{2-} + 2H^+. \quad (2)$$

The acidity of coordinated water molecules increases as the electron transfer within the M–O bond increases. In dilute solutions this leads to a whole set of solute species ranging from aquo-cations $[M(OH_2)_N]^{Z+}$ (h=0) to neutral hydroxides $[M(OH)_Z]^0$ (h=z) or even oxo-anions $[MO_{N'}]^{(2N'-z)-}$ when all protons have been removed from the coordination sphere of the metal [4]. The hydrolysis ratio increases with the pH of the solution and the oxidation state of the metal cation (Fig. 1).

- Large low-valent cations (Na^+, K^+, Cs^+, Ba^{2+}, etc.) exhibit a low polarizing power. Their electronegativity and Lewis acidity are weak. Only electrostatic interactions are involved in solvation, and water molecules in the first coordination sphere are very labile (k=10^9–10^{10} s^{-1}). Their mean lifetime is less than 10 ps and deprotonation does not occur. Only aquo-species $[M(OH_2)_N]^+$ where N~6–8 are observed that cannot be deprotonated even at high pH. The corresponding oxides behave as bases when dissolved in water.

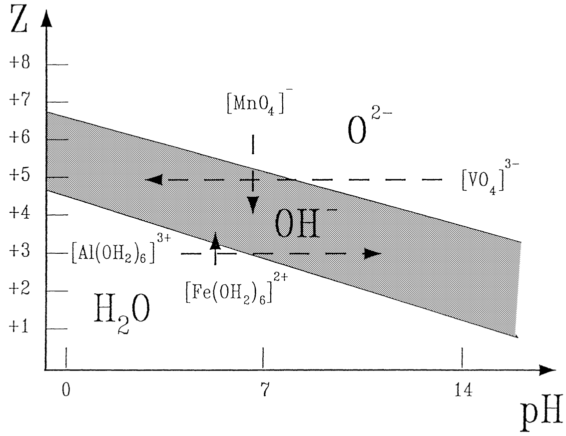


Fig. 1. Charge–pH diagram showing two lines corresponding to h=1 and h=$2N$−1 separating three domains in which H_2O, OH^- or O^{2-} ligands are formed [5].

- Small high-valent metal cations (z>4) attrack electrons very strongly so that aquo-species $[M(OH_2)_N]^{Z+}$ cannot be observed even at low pH. Small electronegative elements at the upper right of the periodic table (P^V, S^{VI}, Cl^{VII}) or highly charged d^0 metal cations (Cr^{VI}, Mn^{VII}) give covalent tetrahedral oxo-anions $[MO_4]^{(8-z)-}$ at high pH. The corresponding oxides behave as acids when dissolved in water.

2.2. Hydrolysis of metal cations

In very dilute aqueous solutions, metal cations exhibit several hydrolyzed monomeric species in the pH range 0–14. The problem would be to be able to predict the chemical nature of these aqueous species at a given pH [6].

Following the electronegativity equalization principle it can be stated that deprotonation (Eq. (1)) goes on until the electronegativity χ_h of hydrolyzed species $[M(OH)_h(OH_2)_{N-h}]^{(z-h)+}$ becomes equal to the mean electronegativity χ_{aq} of the aqueous solution. According to thermodynamics, the chemical potential of protons varies linearly with pH:

$$\mu_{H^+} = \mu^0_{H^+} - \beta pH, \quad \text{where } \beta = 2.3RT. \quad (3)$$

Proton exchange reactions between H_3O^+ and H_2O are very rapid in aqueous solutions so that it can be assumed that χ_{H^+}=χ_{aq}. As a consequence a linear relationship can also be established between the mean electronegativity χ_{aq} and the pH of aqueous solutions.

$$\chi_{aq} = \chi_{aq}^{0} - \lambda\,\mathrm{pH}. \tag{4}$$

χ_{aq}^{0} and λ depend on the reference state for proton and the electronegativity scale. Choosing $[H_5O_2]^+$ (χ=2.732) as a reference for proton at pH=0 and χ=2.49 as the mean electronegativity of water at pH=7 leads to

$$\chi_{aq} = 2.732 - 0.035\,\mathrm{pH}. \tag{5}$$

The mean electronegativity χ_h of hydrolyzed precursors can then be calculated as a function of pH and the hydrolysis ratio h is deduced from the partial charge model.

The charge of hydrolyzed species $[M(OH)_h(OH_2)_{N-h}]^{(z-h)+}$ is

$$z - h = \delta_M + N\delta_O + (2N - h)\delta_H, \tag{6}$$

$$h = [z - \delta(M(OH_2)_N)]/[1 - \delta_H]. \tag{7}$$

The hydrolysis ratio h can be expressed as a function of the partial charges $\delta_i=\sigma_i(\chi_{aq}-\chi_i)$ which depend on the mean electronegativity χ_{aq} of the aqueous solution.

At a given pH, h mainly depends on the oxidation state z and the coordination number N of the cation M^{Z+}.

2.3. *Hydrolysis of* Si^{IV}, Al^{III} *and* V^{V}

- The polarizing power of tetravalent cations (Si^{IV}, Ti^{IV}, Zr^{IV}) is too strong for aquo-species to be formed, even at low pH. They usually give aquo-hydroxo, hydroxo, oxo-hydroxo or oxo species in aqueous solutions. For Si^{IV} (χ_{Si}=1.74, N=4), the partial charge model leads to four different hydrolyzed precursors $[H_nSiO_4]^{(4-n)}$, ranging from $[Si(OH)_3(OH_2)]^+$ (h=3) at pH=0 to $[SiO_2(OH)_2]^{2-}$ (h=6) at pH=14 (Fig. 2(a)).
- In the case of Al^{III}, the coordination of the metal cation decreases from octahedral to tetrahedral as the pH increases. In the M–OH_2 bond, the negatively charged oxygen atom shares electrons with both the metal M and hydrogen: $M\delta^+ \Leftarrow O^{\delta-} \Rightarrow H^{\delta+}$. As deprotonation goes on, electrons are more attracted by the metal. The partial charge δ_M decreases and the M–O bond becomes less polar leading to the covalent anion $[AlO_4]^{5-}$. Octahedral aluminum $[Al(OH_2)_6]^{3+}$ species are observed below pH 3 whereas tetrahedral aluminates $[Al(OH)_4]^-$ are formed above pH 11 (Fig. 2(b)). This coordination change occurs around pH~6 when the partial charge of coordinated water molecules is close to zero.
- In the case of high-valent small cations with empty d orbitals (V^V, Mo^{VI}, W^{VI}), strong $d\pi$–$p\pi$ transfers favor the formation of M=O double bonds. This decreases the positive charge of the metal ion and spontaneous internal proton transfer is observed between two OH groups bonded to the same metal atom giving rise to oxo-aqueous species such as $[VO_2(OH_2)_5]^+$ at low pH rather than $[V(OH)_4(OH_2)_2]^+$ (Fig. 3).

3. Condensation of hydroxylated precursors

Monomeric species can usually be observed in very dilute solution only ($c<10^{-4}$ mol l^{-1}). Condensation reactions often occur at higher concentrations. They proceed via the nucleophilic attack of $HO^{\delta-}$ groups onto metal cations $M^{\delta+}$. Two different pathways, substitution or addition, are followed depending on whether the maximum coordination of the metal cation is already satisfied or not. In all cases, at least one nucleophilic OH group has to be present in the coordination sphere of the hydrolyzed precursor.

The "charge-pH" diagram is then a very useful guide for sol–gel chemistry as condensation only occurs within the OH domain (Fig. 1). Condensation is usually initiated via acid–base reactions by adding a base to low-valent aquo-cations or an acid to high-valent oxy-anions.

The size of condensed species depends on many parameters such as pH, concentration or temperature, the main one being the hydroxylation ratio l=OH/M. As a general rule the condensation of charged precursors remains always limited to oligomeric solute species, polyanions or polycations, that usually contain less than 20 metal atoms. Solid phases can be precipitated from these charged species by adding counter ions in order to form a neutral salt. The precipitation of oxides or hydroxides only occurs from neutral precursors in order to avoid electrostatic repulsion between reactive species.

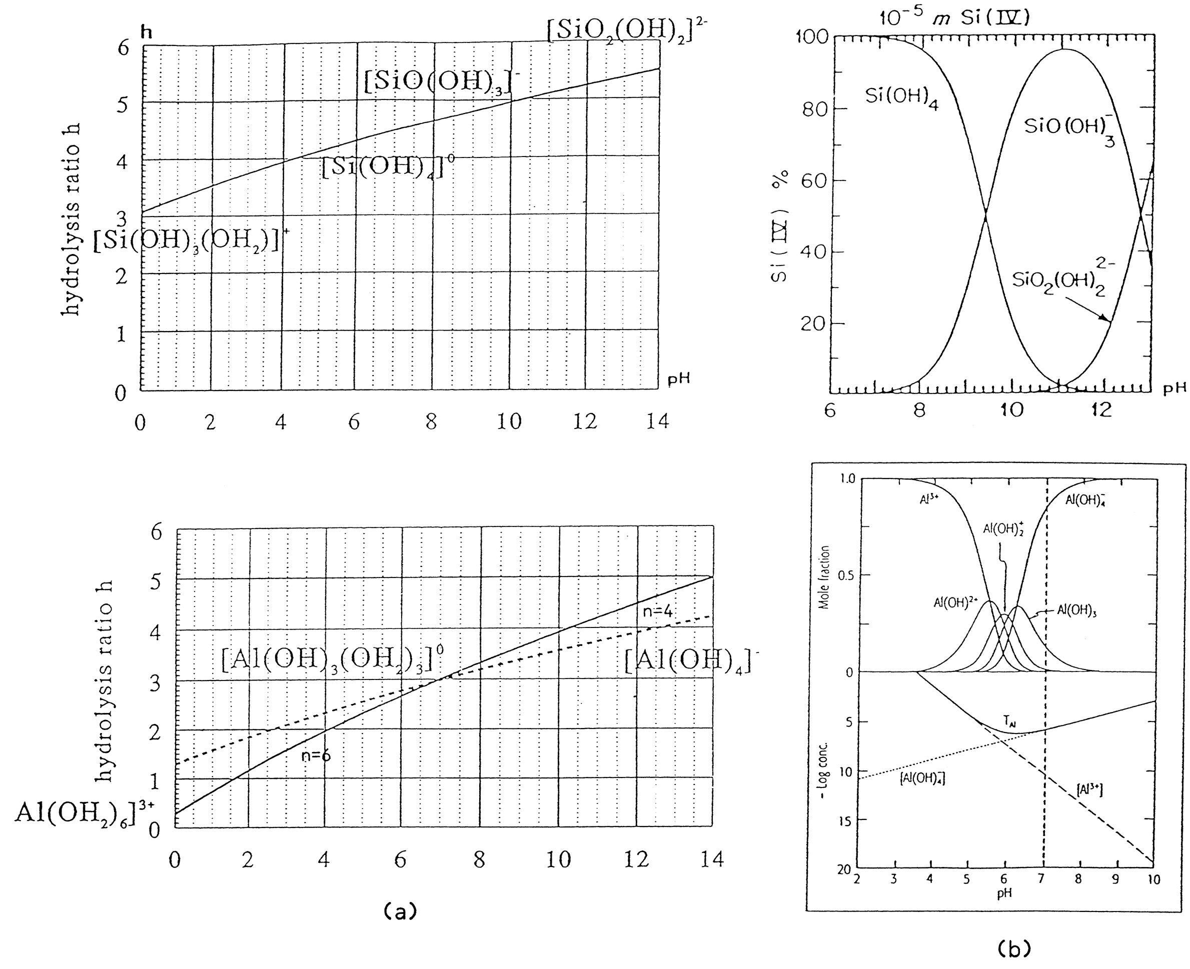


Fig. 2. Hydrolysis of Si^{IV} (N=4) and Al^{III} (N=6, N'=4) in dilute aqueous solutions (a) from the partial charge model, and (b) from thermodynamic data.

3.1. Olation and oxolation

The two main mechanisms for condensation are called olation and oxolation. In both cases, polynuclear species are formed via the elimination of water molecules from the coordination sphere of the metal cation containing at least one M–OH group [2,6].

1. Olation corresponds to the nucleophilic addition of a negatively charged OH group onto a positively charged hydrated metal cation. As aquo-cations already exhibit their maximum coordination number, the formation of an "ol" bridge requires the departure of one water molecule:

$$-\text{M}-\text{OH}+\text{H}_2\text{O}-\text{M}- \Rightarrow \text{M}-\text{OH}-\text{M}-+\text{H}_2\text{O}.$$

This reaction is usually governed by the lability of the M–OH_2 bond which increases when the size of the cation increases and its oxidation state decreases. Olation should then follow a dissociative SN_1 mechanism and olation reactions are usually very fast. They actually correspond to the coordination expansion of OH groups from terminal to bridging μ_2-OH or μ_3-OH. A more complex mechanism should be involved with transition metal cations for which crystal field stabilization effects could be important (Cr^{3+},

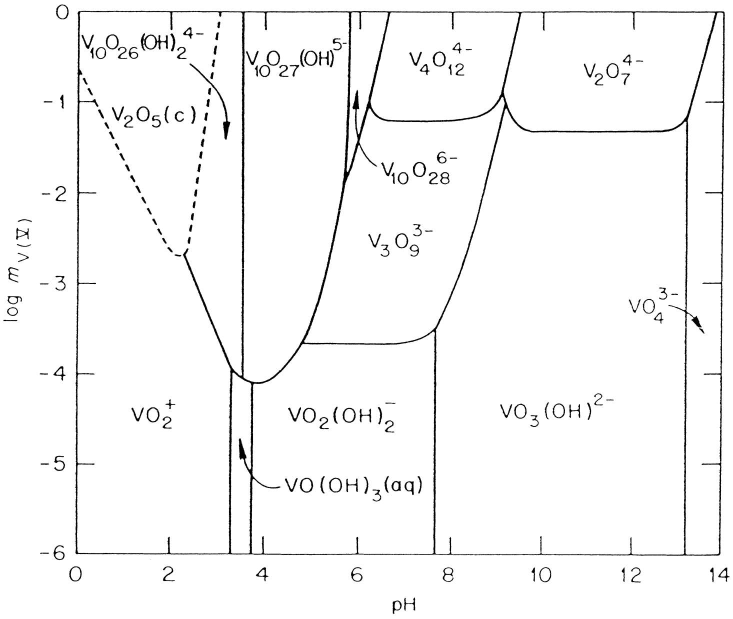
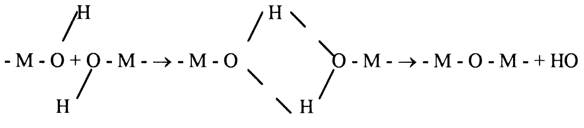


Fig. 3. V^V species in aqueous solution as a function of pH and concentration [7].

Ni^{2+}). The very low lability of coordinated water molecules then allows the formation of bridging $H_3O_2^-$ ligands involving a hydrogen bond between a hydroxo ligand of one metal atom and an aquo ligand of another one with a characteristic distance of about 5 Å. These bridging ligands are not very stable and transform into "ol" bridges upon moderate heating or even aging [8].

2. Oxolation occurs with precursors that do not contain any water molecule coordinated to the metal cation. It involves the condensation of two OH groups to form one water molecule which is then removed giving rise to an "oxo" bridge. This proceeds via an associative SN2 mechanism as follows:


$$-M-\overset{H}{O}+\underset{H}{O}-M-\rightarrow -M-O\overset{H}{\diagdown}\underset{H}{\diagdown}O-M-\rightarrow -M-O-M-+\mathrm{HO}$$

This reaction could be described as the dehydration of olated species via the formation of one water molecule between two hydrogen bonded OH groups. It is catalyzed by acids which favor the protonation of the leaving water molecule.

Olation requires the presence of at least one coordinated water molecule and involves mainly low-valent cations ($z<4$) in aquo-hydroxo precursors whereas oxolation rather concerns high-valent cations. When both mechanisms compete, it appears that olation is always faster than oxolation.

The formation of condensed species requires at least one OH group ($\delta_{OH}<0$) in the coordination sphere of the precursor, but the positive charge of the metal cation $M^{\delta+}$ has also to be high enough ($\delta>+0.3$) for nucleophilic reactions with OH to be possible. A very interesting example is the aqueous chemistry of phosphates. Despite many similarities between the structure of silicates and phosphates in the solid state, their solution chemistry is quite different. This arises from the high polarization power of P^V which strongly attracks electrons within P–O bonds lowering the positive charge of P. Polyphosphates cannot be formed in aqueous solutions at room temperature via the condensation of monomeric precursors $[H_nPO_4]^{(3-n)-}$. H_3PO_4 is a strong acid while the positive charge of P^V is too small in $[H_2PO_4]^-$ and $[HPO_4]^{2-}$. Polyphosphates are usually prepared by thermal dehydration. They are not stable toward hydrolysis in aqueous solutions and their hydrolysis rate increases as the number of P atoms increases and pH decreases.

3.2. Condensation of $\mathrm{Al^{III}}$

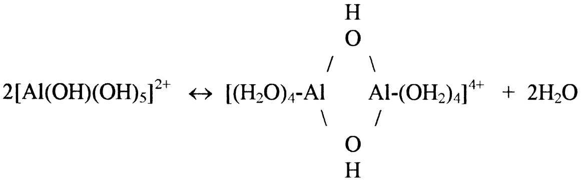
3.2.1. Formation of polycations

Aquo-cations $[\mathrm{Al(OH_2)_6}]^{3+}$ are formed below pH~3. Condensation can be initiated by increasing the pH. Coordinated water molecules are very labile and condensation follows an olation mechanism. Olated polycations are formed during the first steps of condensation [9,10].

Only few polycations are known for Al^{3+}. The first hydroxylation stages (1=OH/Al<2) lead to the formation of $[\mathrm{Al(OH)(OH_2)_5}]^{2+}$ and $[\mathrm{Al(OH)_2(OH_2)_4}]^{+}$. Olation then leads to oligomeric species in equilibrium with monomers (Fig. 4). The $[\mathrm{Al_2(OH)_2(OH_2)_8}]^{4+}$ dimer and a more or less deprotonated cyclic trimer $[\mathrm{Al_3(OH)_{4+\mathit{x}}(OH_2)_{9-\mathit{x}}}]^{(5-x)+}$ have been evidenced by potentiometric methods and NMR (^{27}Al, ^{17}O). The well known $\mathrm{Al_{13}}$ polycation $[\mathrm{Al_{13}O_4(OH)_{24}(OH_2)_{12}}]^{7+}$, which has been extensively used for the synthesis of the so-called ‘pillared clays’, is formed upon further hydrolysis (1~2.5). It is made of one tetrahedral $[\mathrm{AlO_4}]$ surrounded by four groups of three octahedral $[\mathrm{AlO_6}]$.

The first condensation steps of trivalent aquo-cations $[\mathrm{M(OH_2)_6}]^{3+}$ were clearly evidenced with $\mathrm{Cr^{3+}}$ which gives inert complexes because of crystal field stabilization effects. They could be described as follows [11]:

The dimerization of the h=1 $[\mathrm{Al(OH)(OH_2)_5}]^{2+}$ precursor leads to edge sharing dimers (Fig. 4).



$$2[\mathrm{Al(OH)(OH)_5}]^{2+} \leftrightarrow [(\mathrm{H_2O})_4\text{-Al}\begin{array}{c}\mathrm{H}\\ \mathrm{O}\\ / \quad \backslash\\ \\ \backslash \quad /\\ \mathrm{O}\\ \mathrm{H}\end{array}\mathrm{Al\text{-}(OH_2)_4}]^{4+} + 2\mathrm{H_2O}$$

Further hydrolysis leads to trimeric species formed by adding one hydrolyzed monomer (h=2) to the previous dimer.

$$[\mathrm{Al_2(OH)_2(OH_2)_8}]^{4+} + [\mathrm{Al(OH)_2(OH_2)_4}]^{+}$$
$$\Rightarrow [\mathrm{Al_3(OH)_4(OH_2)_9}]^{5+} + \mathrm{H_2O}.$$

Such trimeric species are often observed in aqueous solutions of polyanions or polycations. They exhibit a

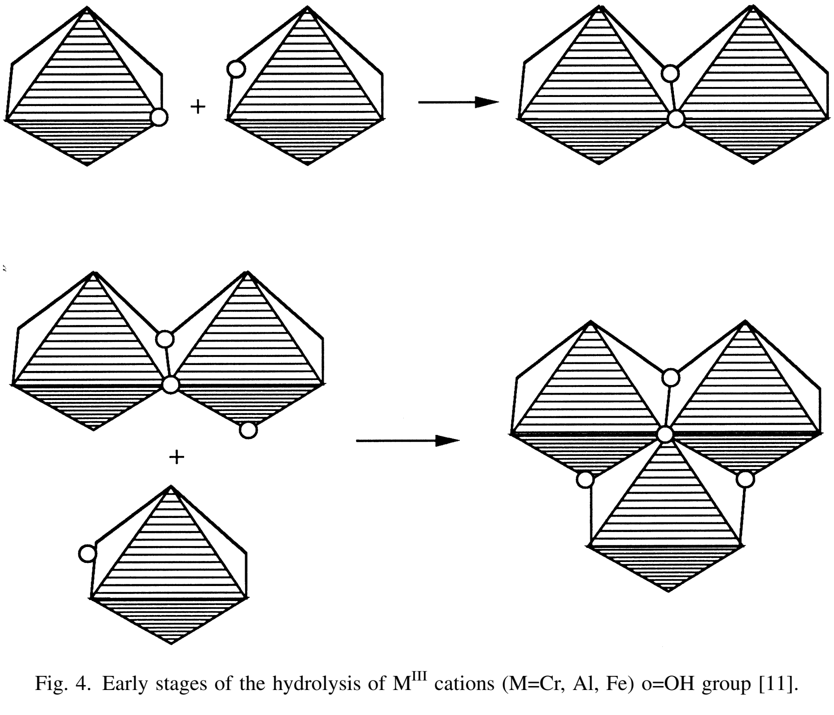


Fig. 4. Early stages of the hydrolysis of $\mathrm{M^{III}}$ cations (M=Cr, Al, Fe) o=OH group [11].

compact cyclic structure in order to minimize electrostatic repulsion between cations in edge-sharing adjacent $[MO_6]$ octahedra. $[Al_3(OH)_4(OH_2)_9]^{5+}$ trimers cannot be isolated in aqueous solutions, but their citric derivative has been precipitated as single crystals. Al^{3+} ions are bonded to a central μ_3-OH group. Electrons are strongly attracted by the small and highly polarizing $A1^{3+}$ ions, making the μ_3-OH group highly acidic and therefore easily deprotonated.

$$[Al_3(OH)_4(OH_2)_9]^{5+} + H_2O \Rightarrow [Al_3O(OH)_3(OH_2)_9]^{4+} + H_3O^+.$$

A nucleophilic oxygen atom is formed which can react with positive $[Al(OH_2)_6]^{3+}$ species. The nucleophile addition of four deprotonated trimers onto a single aquo-ion leads to the formation of the $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ polycation.

Several features have to be pointed out about these polycations.

- Bridging OH groups tend to get their highest coordination (μ_3-OH). Therefore, all polycations, even the large ones, exhibit a compact structure. Trimeric units $[M_3O_{13}]$ with a central μ_3-OH bridge are therefore often found in polycations and polyanions whereas chain oligomers formed via μ_2-OH bridges are never observed.
- The molecular complexity of polycations increases with the hydroxylation ratio 1, but the condensation of these positively charged species remains always limited to rather small oligomers. This should be due to the fact that the nucleophilic power of OH groups decreases as they form more bonds (OH>μ_2-OH>μ_3-OH) and the positive charge of the polycation increases. Therefore polycations cannot be considered as secondary building units (SBU) for the formation of solid phases and it is not possible to predict a priori the condensation degree of a polycation.

3.2.2. *Formation of solid phases*

3.2.2.1. Room temperature precipitation via base addition Adding a base to an aqueous solution of $A1^{3+}$ leads to different solids according to the pH of precipitation. A gelatinous amorphous precipitate is formed around pH~7 that leads to crystalline hydroxides upon aging at room temperature. These hydroxides (bayerite or hydrargillite) are made of layers of edge sharing $[Al(OH)_6]$ octahedra and remain stable toward dehydration at room temperature.

The crystalline hydroxide is not formed directly from the neutral monomeric precursor $[Al(OH)_3(OH_2)_6]^0$. Strong pH gradients occur when the base is added to the aqueous solution, allowing the formation of several solute species.

A straightforward analysis of the structure of $Al(OH)_3$ shows that it cannot be formed via the association of the neutral trimeric polycations previously described. However rather inert species such as Al_{13} could withstand neutralization and can actually be found in the amorphous gel. It has been shown that adding a base to a solution of this polycation gives an amorphous precipitate that, upon aging leads to bayerite.

Several chemical species seem to be mixed in the amorphous gel and crystallization should result from a progressive reorganization. This can be done either via the in situ reorganization of the solid phase or via a dissolution–crystallization process.

- In situ reorganization is favored when the pH of the solution is close to the solubility minimum of the solid, between pH 8 and 10, around the point of zero charge (PZC). Oxolation leads to partial dehydration and the formation of the pseudoboehmite γ-AlOOH (Fig. 5(a)).
- Dissolution and recrystallization via the solution often leads to particles much larger than the former ones. It occurs when the pH is far from the PZC and should be responsible for the crystallization of bayerite below pH 7.5. At high pH (~12), monomeric tetrahedral species $[Al(OH)_4]^-$ and $[Al(OH)_3(OH_2)]^0$ could lead to bayerite via the addition of neutral precursors.

3.2.2.2. Precipitation via thermohydrolysis The enthalpy variation for hydrolysis is positive and often close to the enthalpy of dissociation for water (1 3.3 kcal/mol). Hence the deprotonation of coordinated water molecules can be performed upon heating aqueous solutions. In these conditions, Al^{3+} solutions lead directly to the precipitation of γ-AlOOH. However the mechanism for the formation of boehmite should be rather different from that observed

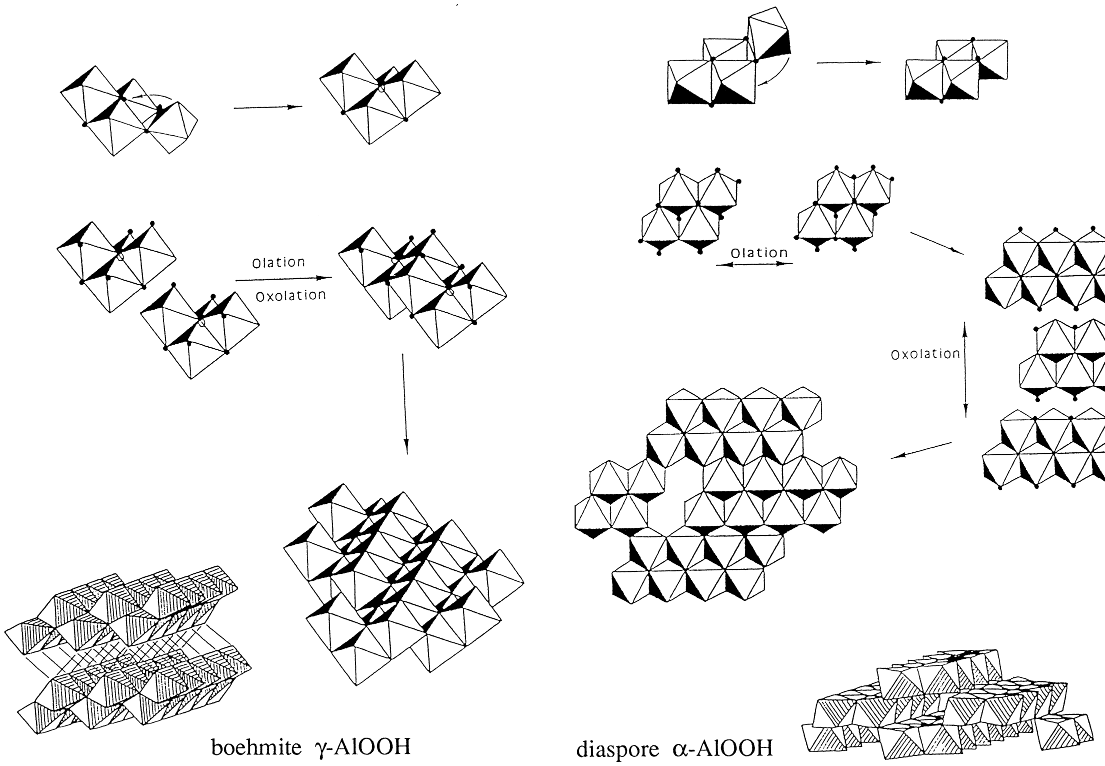


Fig. 5. Suggested mechanisms for the formation of AlOOH from tetrameric builing blocks: (a) boehmite γ-AlOOH at room temperature and (b) diaspore α-AlOOH under hydrothermal conditions.

upon aging at room temperature. OH groups are progressively formed in situ and condensation could follow the same mechanism as observed for polycations. The key point would be the formation of tetramers from trimeric species $[Al_3(OH)_9(OH_2)_4]$. The deprotonation of the acidic μ_3-OH group leads to a μ_4-O bridge and the formation of a skewed tetramer (Fig. 5(a)). Olation and oxolation then lead to the layered structure of boehmite. Heating also increases condensation kinetics and favors dehydration leading to AlOOH rather than $Al(OH)_3$.

3.2.2.3. Hydrothermal synthesis of $\alpha-$AlOOH

Under hydrothermal conditions, the properties of water as a solvent are deeply modified. The dielectric constant decreases and the acidity scale is reduced. At moderate temperatures, hydrothermal synthesis leads to the same solid phases (boehmite) as thermohydrolysis. Precursors are usually solids rather than solutions and the shape and size of the final solid particles are different. At high temperature, around 400°C, diaspore α-AlOOH is obtained. This may be due to the weaker acidity of the μ_3-OH bridge arising from the low dielectric constant of water. μ_3-OH bridges are formed leading to planar, rather than skewed, tetramers (Fig. 5(b)).

3.3. Condensation of Si^{IV}

3.3.1. Formation of polyanions

Si^{IV} remains tetrahedrally coordinated over the whole range of pH. Condensation occurs upon acidification of aqueous solutions of silicates. Condensed phases are made of corner sharing $[SiO_4]^{4-}$ tetrahedra in order to minimize electrostatic repulsion between cations.

Monomeric species, $[H_2SiO_4]^{2-}$, are observed under very alkaline conditions only ([OH]$\sim$6 M).

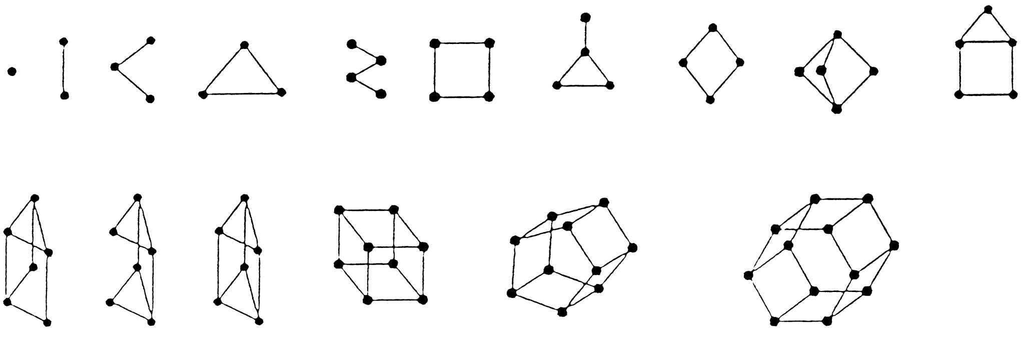


Fig. 6. Some oligomeric silicate species characterized by ^{29}Si NMR.

Around pH$\sim$12, oxolation occurs between $[H_2SiO_4]^{2-}$ and $[H_3SiO_4]^{-}$ giving rise to a large number of anionic oligomers. The dimeric anion $[Si_2O_3(OH)_4]^{2-}$ is formed around $[OH]\sim2$. The cyclic trimer $[Si_3O_3(OH)_3]^{3-}$ is observed below this value, the cyclic tetramer $[Si_4O_8(OH)_4]^4$ at pH$\sim$14, then oligomers containing 5–8 silicon atoms are in equilibrium with orthosilisic acid.

Actually about 20 different species ranging from monomers to decamers have been evidenced by ^{29}Si NMR in aqueous solutions of potassium silicate. Q^4 species (linked to four other SiO_4 tetrahedra) are never observed above pH 9 and most polysilicates are highly branched or cyclic (Fig. 6). Linear oligomers are no more observed beyond four Si atoms [12].

This can be qualitatively understood if we consider a chain trimer $[Si_3O_{10}]^{8-}$. The Q^2 Si atom, with two μ_2-O bridges, is more positively charged than Q^1 Si atoms which are bonded to three terminal OH groups. Therefore condensation occurs via the nucleophile attack of the Q^2 Si atom leading to branched, rather than chain, oligomers. Cyclization usually occurs so that only rather small oligomers are formed in an alkaline solution.

Moreover, as all these species are negatively charged, cations have to be involved in the formation of solid phases. Therefore the chemical nature of counter cations in the solution has a strong effect on the formation of these oligomeric species. Cage polysilicates for instance are formed in the presence of alkyl ammonium ions such as $[N(CH_3)_4]^+$ whereas cycles are observed with Na^+. This might be a key point for the hydrothermal synthesis of zeolites in the presence of templates [13].

3.3.2. Formation of solid phases

Tetrahedral $[H_nSiO_4]^{(4-n)-}$ precursors do not have any coordinated water molecule so that condensation must occur via oxolation.

- In the pH range 3<pH<9, neutral $[Si(OH)_4]^0$ is the major precursor and oxolation leads to the formation of amorphous hydrated silica gels:

  $$Si(OH)_4 \rightleftharpoons SiO_2 + 2H_2O.$$

  Gelation is very slow and goes through a minimum around pH$\sim$3. Reaction rates increase significantly by changing the pH. This is rather unusual as solid phases generally form faster when neutral species are largely predominant. This points out the importance of catalysis for oxolation reactions. Each step of the oxolation reaction (nucleophilic attack and water departure) has its own activation energy.
- Base catalysis occurs at pH>3. Anionic precursors $[SiO(OH)_3]^-$ are better nucelophiles than $[Si(OH)_4]^0$ increasing the rate of the nucleophilic addition. This reaction is directed toward the most positively charged Si atoms (Q^2) leading to branched species. Gelation occurs readily around pH 7–8. Large colloidal particles are formed (few 100 Å in diameter) and dense opaque gels are obtained (Fig. 7). Condensation between surface OH groups then leads to fast aggregation and the formation of unstable gels made of more or less dense particles. Upon drying these gels give highly porous silica.
- Acid catalysis below pH$\sim$3 leads to the protonation of the leaving silanol groups. This concerns

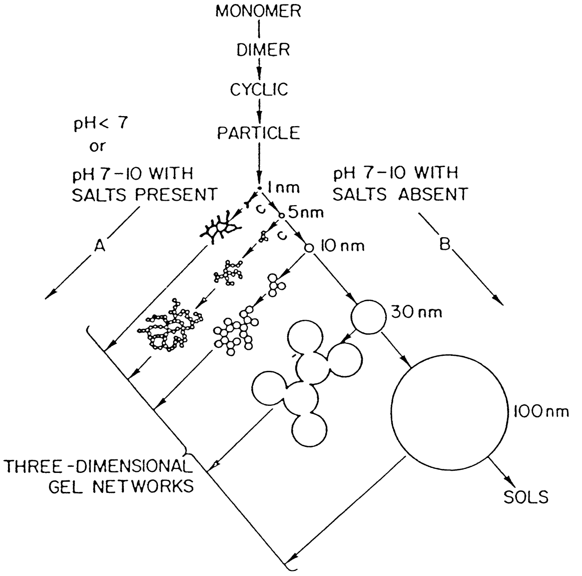


Fig. 7. Polymerization of silica in basic and acid conditions [12].

mainly terminal Si–OH groups rather than the bridging ones, leading to the formation of chain polymers (Fig. 7).

- Si^{IV} is known to be a very good glass former and crystalline silica is never obtained at room temperature from aqueous solutions. Crystalline phases (quartz or cristobalite) are formed at very high temperature. Crystalline compounds, such as clays or zeolites, in which $[SiO_4]^{4-}$ behaves as a complexing-bridging group, are obtained in the presence of cations such as Al^{3+}.

3.3.3. *Formation of alumino-silicates*

Silicate anions react with Al^{III} precursors to give alumino-silicate compounds [13]. These reactions are currently used for the synthesis of zeolites. Usually a gel is formed when mixing the silica and alumina sources.

- In alkaline solutions Al^{III} gives negatively charged tetrahedral $[Al(OH)_4]^-$ species, a structure consistent with its incorporation into a zeolite framework. Because of the lower charge of Al^{III} compared to Si^{IV}, counter cations such as Na^+ or $[N(CH_3)_4]^+$ have to be added for charge compensation. They are known to play a major role in the formation of the zeolite structure.
- At lower pH, when F^- is used as a mineralyzer instead of OH^- for instance, aluminum precursors can give positively charged octahedral species. The formation of alumino-silicates could then be described as the complexation of cationic Al species by silicate anions.

3.4. *Condensation of* V^V

3.4.1. *Formation of polyanions*

The aqueous chemistry of high-valent cations such as V^V, Mo^{VI} and W^{VI} is dominated by the formation of polyoxometallates that exhibit compact, highly symmetrical molecular structures [14]. A large variety of V^V species can be found in aqueous solutions. At room temperature they mainly depend on vanadium concentration and pH (Fig. 8). Monomeric orthovanadate $[VO_4]^{3-}$ is the main species at very high pH and there is no evidence for condensed vanadates at pH=14.

Condensation of the protonated $[HVO_4]^{2-}$ anion via oxolation gives pyrovanadates $[V_2O_7]^{4-}$ and then metavanadates $[V_4O_{12}]^{4-}$ as the pH decreases. In all these polyanions, V^V remains tetrahedrally coordinated. Condensation proceeds via substitution oxolation reactions leading to cycles or chains made of corner sharing $[VO_4]^{3-}$ tetrahedra (Fig. 8). Coordination expansion, from four to six, occurs around $H^+/V\sim2.5$. This can be easily evidenced by the orange coloration due to charge transfer electronic transitions. Decavanadate species $[V_{10}O_{27}(OH)]^{5-}$ are observed in the pH range 5–3 where the neutral precursor $[VO(OH)_3]^0$ begins to be formed. The mean negative charge of these anionic species decreases as condensation increases down to the point of zero charge (pH$\sim$2). Below that pH value, monomeric cationic species $[VO_2]^+$ are formed in which V^V is sixfold coordinated [7,14].

As for polycations, the condensation of polyanions remains always limited, leading to solute compact species. With tetrahedral VO_4 units, only corner sharing polyanions can be formed, leading to short chains or cycles. Octahedral unit MO_6 can share edges and μ-oxo bridges tend to adopt the highest possible coordination. In order to decrease electrostatic repulsion between highly charged cations, V^V are shifted toward a terminal oxygen (V=O bond) leading to strongly distorted VO_6 octahedra in which V–O distances range from 1.6 to 2.3 Å. The basicity of these terminal

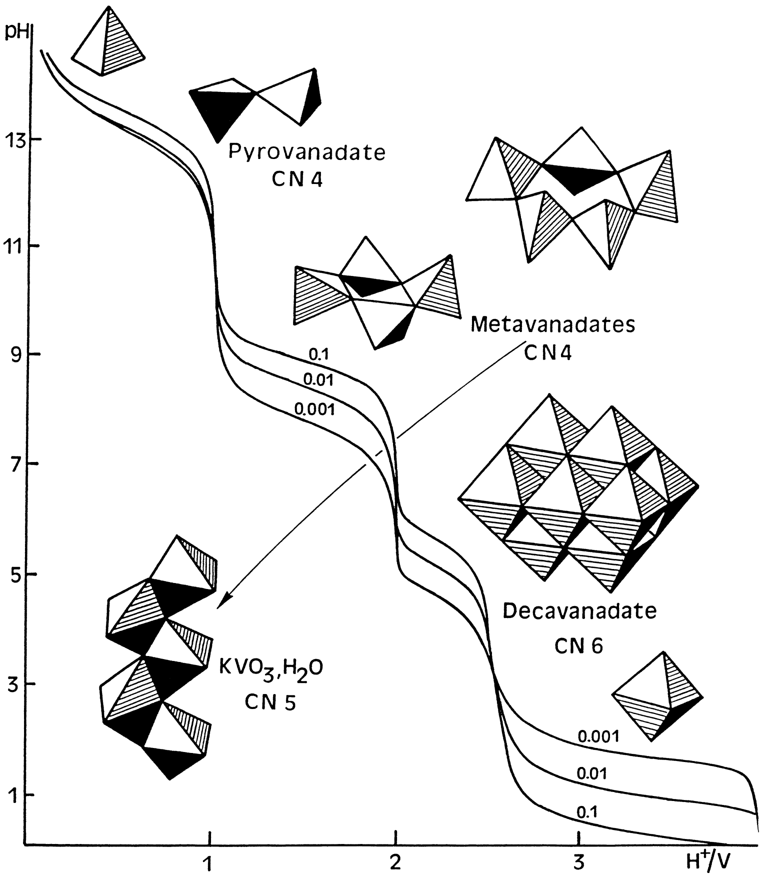


Fig. 8. V^V species formed in aqueous solutions.

V=O oxygen atoms is too small for protonation to occur and condensation stops at this stage.

3.4.2. *Formation of* V_2O_5, nH_2O *gels*

Vanadium pentoxide gels can be synthesized via the acidification of aqueous solutions of sodium metavanadate $NaVO_3$. Protonation is usually obtained by adding an acid to aqueous solutions of vanadate salts but it can be better performed via a proton exchange resin so that counter anions or cations are removed from the solution. The solution turns yellow as soon as acidification is performed leading to decavanadic acid $[H_2V_{10}O_{28}]^{4-}$. The solution then progressively becomes dark red and its viscosity increases upon aging showing that highly condensed species are formed.

A red–brown xerogel V_2O_5,1.8H_2O is obtained upon drying in air at room temperature. It has been shown that this compound exhibits a layered structure made of V_2O_5 ribbons [15].

As for polycations, decavanadate $[V_{10}O_{26}(OH)_2]^{4-}$ cannot behave as a precursor, or building block, for the oxide network. Neutral species $[VO(OH)_3]^0$, arising from the dissociation of decavanadic acid at low pH should then be considered as molecular precursors:

$$[V_{10}O_{26}(OH)_2]^{4-} + 4H_3O^+ + 28H_2O$$
$$\Leftrightarrow 10[VO(OH)_3(OH_2)_2]^0.$$

In this precursor, vanadium is sixfold coordinated with one water molecule along the *z* axis, opposite to

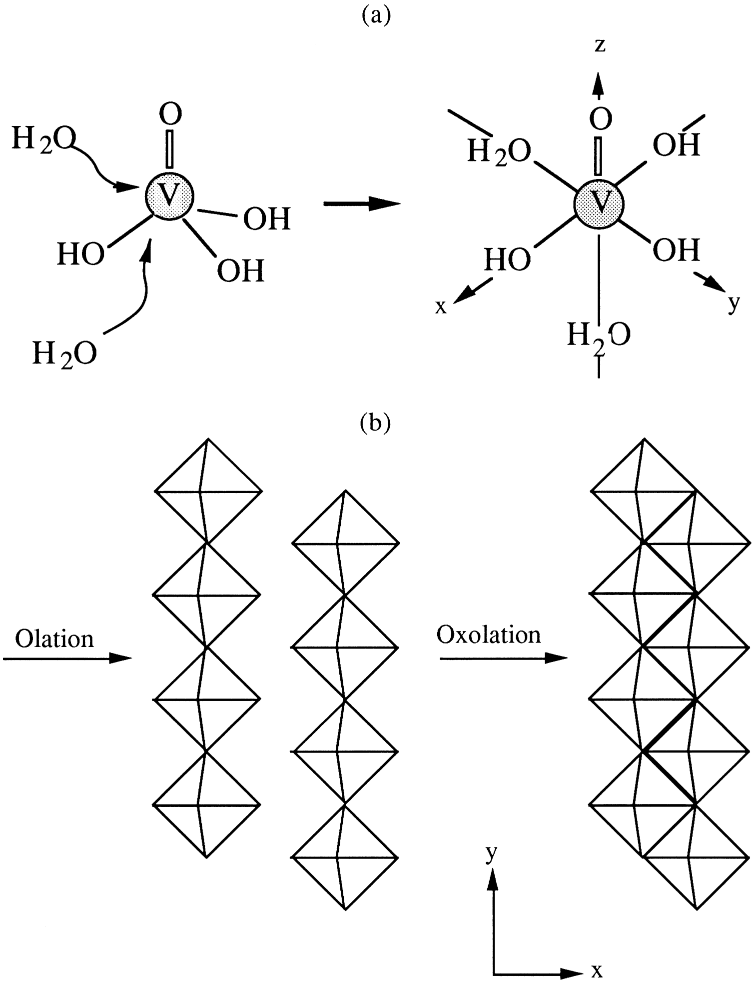


Fig. 9. Suggested mechanism for the formation of V_2O_5, nH_2O gels: (a) coordination expansion and (b) condensation.

the short V=O double bond and another one in the equatorial plane, opposite to an OH group (Fig. 9(a)). One V–OH_2 and three V–OH bonds are formed in the equatorial plane so that x and y directions are not equivalent. Fast olation reactions should occur first along the H_2O–V–OH direction. This leads to the formation of corner-sharing olated chain polymers. Slower oxolation reactions transform μ_2-OH bridges into μ_3-O bridges forming double chains. Further oxolation involving the last OH groups links these double chains together via μ_2-O bridges so that ribbon-like fibers are formed in agreement with experimental data (Fig. 9(b)).

4. Complexation and chemically controlled condensation

The formation of condensed phases from aqueous solutions is mainly governed by the pH of the solution. However most aqueous systems also contain counter ions introduced during the dissolution of inorganic salts in water. Foreign ions (anions or cations) are also often added in order to improve the process and obtain the desired products. Such ions, even when added in small amount, can change the coordination sphere of solute precursors (complexation) and therefore control their reactivity toward condensation. The morphology, structure and even chemical composition of the resulting solid particles can be modified via complexation [16,17].

Spherical hematite particles (α-Fe_2O_3) are obtained when aqueous solutions of $FeCl_3$ are heated under reflux while acicular particles are formed with $Fe(NO_3)_3$ in the presence of phosphate ions. Goethite (α-FeOOH) is precipitated from $Fe(NO_3)_3$ while Akaganeite (β-FeOOH) is obtained with $FeCl_3$. The thermohydrolysis of $Ti(SO_4)_2$ aqueous solutions leads to anatase TiO_2 while the rutile phase is formed in the presence of chloride or nitrate. Cationic templates are widely used for the hydrothermal synthesis of zeolites. Zeolite A, sodalite and cancrinite tend to form in aqueous Na^+ media while zeolites with low Al content are favored by large cations such as tetraalkylammonium (R_4N^+).

These examples show that anions (or cations) can play an important role in the formation of condensed phases from aqueous solutions. They have therefore to be taken into account in the description of hydrolysis and condensation reactions.

4.1. Complexation of cationic precursors

Negatively charged anions X^{x-} can react with cationic precursors (and vice versa) to give metal complexes. For monovalent anions, the reaction can be written as follows:

$$[M(OH_2)_N]^{z+} + xX^- \Leftrightarrow [M(X)_x(OH_2)_{N-\alpha x}]^{(z-x)+} + \alpha x H_2O.$$

α corresponds to the number of water molecules which are replaced by X^-, α=1 for monodentate ligands such as Cl^- and α=2 for bidentate ligands such as $(SO_4)^{2-}$. Complexation leads to the formation of new precursors and the whole hydrolysis–condensation process can be modified. Basic salts in which both X^- anions and OH groups are present can even be obtained when the complexing anion is not removed during the nucleation and growth of solid phases.

Many data can be found in literature about the formation of monomeric complexes but very little is known about the complexation of oligomeric species. Several parameters could be used to describe the stability of these complexes in aqueous solutions, electronegativity and pH seem to be the main ones [5].

- In aqueous solutions, complexes have to avoid both ionic dissociation by the aqueous solvent ($\varepsilon \sim 80$) and hydrolytic dissociation via the nucleophilic substitution by water molecules (Lewis base). Both reactions depend on the extent of electron transfer between metal cation and anion within the M–X bond. As a general rule, anions should be able to give complexes with cationic precursors when their electronegativities are rather close, i.e. when the M–X bond is rather covalent. As all these reactions occur in water this means that the mean electronegativity of anionic species should be close to that of the aqueous solution i.e. $\chi_{H_2O} = \chi_X = 2.5$. Highly electronegative anions such as nitrate NO_3^- or perchlorate ClO_4^- mainly behave as counter anions. They exhibit very poor complexing ability and are usually not involved in the formation of solid phases.
- Complexation in aqueous solutions also depends on pH. Protonation or deprotonation reactions of cationic and anionic species take place when changing the pH. Acetates for instance give CH_3COOH and loose their complexing ability below pH≈4. The observed complexation constant decreases and “M–X” complexes remain stable over a limited range of pH only. As a general rule, the pH at which complexes can be formed shifts toward higher values when the charge M^{z+} of the cation decreases and when the mean electronegativity of the anion decreases. Some anions can be complexing at low pH, at the beginning of the condensation process and become noncomplexing during the nucleation and growth of solid particles. They are then released in the solution.
- Polydentate anions such as $[SO_4]^{2-}$ or $[PO_4]^{3-}$ usually exhibit high complexing abilities. They exhibit several protonated forms and are often complexing over a wide range of pH. They can behave as chelating or bridging ligands and could be considered as network formers, leading to the precipitation of salts, or basic salts, rather than oxides or hydroxides.

4.2. Complexation and condensation of Zr^{IV} precursors

- Anions such as Cl^- (χ=2.3) do not give complexes with Zr^{IV} in an acid medium (pH≈2). When dissolved in water, $ZrCl_4$ is readily hydrolyzed giving rise to $h=2$ species $[Zr(OH)_2(OH_2)_6]^{2+}$. Olation then leads to the well-known cyclic tetramer, $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$ in which Zr atoms are eightfold coordinated by four bridging OH groups and four terminal water molecules. There is no Zr–Cl bond (Fig. 10(a)) [18]. Adding ammonia leads to the precipitation of amorphous hydrous zirconia ZrO_2, nH_2O. However, Cl^- anions become complexing between pH 5 and 9. They are then released at higher pH but a significant amount of anions remain adsorbed in the amorphous oxide. They have to be removed by washing. The amount of Cl^- retained by the precipitate decreases as the final pH of precipitation increases. A change in the final pH from 8 to 10 can alter the crystallization temperature by 200°C and the tetragonal-monoclinic transformation temperature by more than 1000°C. Zirconia can also be obtained via the thermohydrolysis of an acid solution of $ZrOCl_2$ (pH<3). Non-complexing Cl^- anions are not involved in the polymerization process and pure crystalline monoclinic zirconia is obtained [19].

- Phosphates exhibit several protonated forms $[H_nPO_4]^{(3-n)-}$ which are strongly complexing over a large range of pH. They remain bonded to Zr^{IV} all the way during the formation of solid phases giving rise to the precipitation of phosphates rather than oxides. Phosphoric acid reacts with aqueous solutions of Zr^{IV} giving α-$Zr(HPO_4)_2$,H_2O when the solution is refluxed for several hours. This layered phosphate is built up of negatively charged $[Zr(PO_4)_2]_n^{2n-}$ layers in which phosphate groups are bonded to three $[ZrO_6]$ octahedra (Fig. 10(b)) [20].

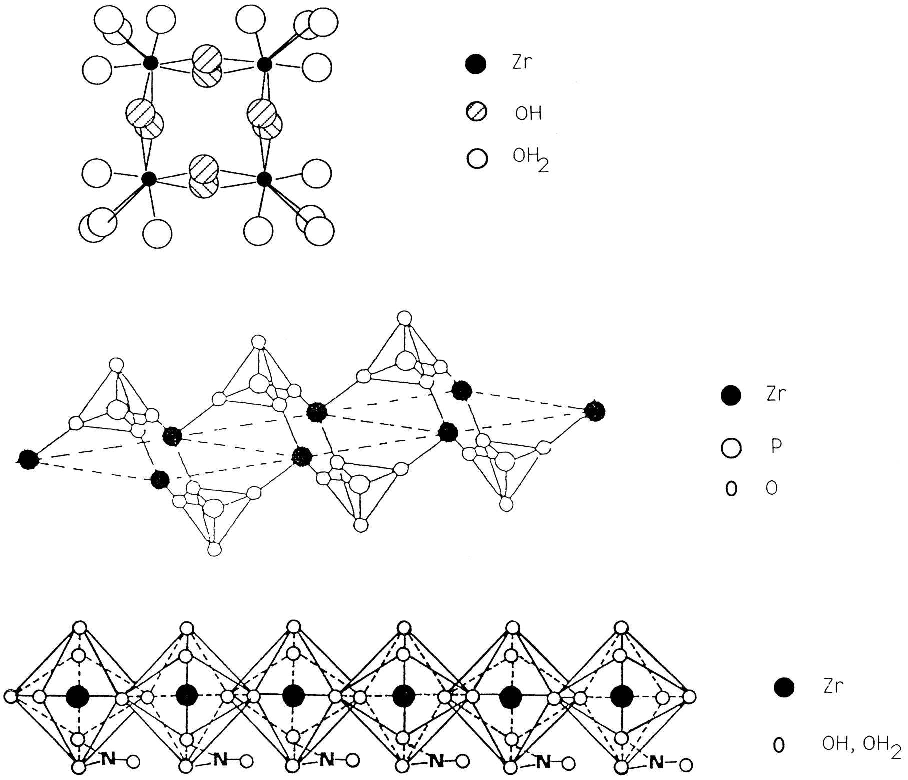


Fig. 10. Solid phases formed via the precipitation of Zr^{IV} precursors: (a) $ZrOCl_2{\cdot}8H_2O$, (b) α-$Zr(HPO_4)_2{\cdot}H_2O$, and (c) $Zr(OH)_2(NO_3)_2{\cdot}4.7H_2O$.

- Nitrates cannot form monodentate complexes with tetrameric zirconium precursors and hydrous zirconia is obtained by adding a base to an aqueous solution of zirconium nitrate. However a basic salt, $Zr(OH)_2(NO_3)_2\cdot 4.7H_2O$, can be precipitated from concentrated zirconium nitrate solutions at low pH. It is made up of $[Zr(OH)_2(OH_2)_2(NO_3)]^+$ chains in which zirconium atoms are eightfold coordinated by four OH groups, two water molecules and one chelating nitrate. These chains are held together by hydrogen bonds through additional water molecules and non-complexing nitrate groups located between the chains (Fig. 10(c)) [21].
- Sulfates $[H_nSO_4]^{(2-n)-}$ form complexes with Zr^{IV} precursors up to pH≈11. They can displace OH groups from hydrolyzed Zr^{IV} species and form sulfate bridges between zirconium atoms. Zirconium sulfate $Zr(SO_4)_2\cdot 4H_2O$ is readily crystallized from sulfuric acid solutions. Many basic zirconium sulfates have been described in which $(SO_4)^{2-}$ groups behave as bridging ligands between zirconium atoms. Moreover sulfate anions can be used to control the precipitation of zirconia. Polydispersed ZrO_2 particles are obtained when an acidic aqueous solution of $ZrOCl_2\cdot 8H_2O$ is refluxed whereas monodispersed spherical ZrO_2 particles are formed in the presence of K_2SO_4. Complexation with $(SO_4)^{2-}$ anions leads to the in situ generation of sulfate complexes which behave as precursors for nucleation. Protons are formed during the process and noncomplexing $(HSO_4)^-$ anions are released at a further stage leading to the precipitation of zirconia free of sulfate.

5. Conclusion

This paper describes the synthesis of metal oxides or hydroxides from aqueous solutions. Chemical mechanisms have mainly been analyzed in the frame of molecular orbital theory and the partial charge model. The chemical reactivity of molecular precursors was described as a function of chemical parameters such as electronegativity and pH. However many other parameters such as temperature and the role of templates should also be taken into account.

- Heating allows a faster diffusion of solute species. The dielectric constant of water decreases drastically when the temperature increases and water looses its properties as a good solvent toward ionic species. Ionic dissociation becomes less important so that ion-pairs and neutral complexes are more often observed.
- Templates are also often used in order to obtain the desired phase. Their role has not been described in this paper. It could be related to the complexation of molecular precursors but weak interactions (van der Waals, hydrogen bond, hydrophilic–hydrophobic interactions, solvation, etc.) should also be involved.

It appears that much work has still to be performed before reaching a complete understanding of the aqueous chemistry of metal cations, from monomeric precursors to oligomeric condensed species and precipitated solid phases.

5.1. The partial charge model

The partial charge model (PCM) is based on the electronegativity equalization principle stated by R.T. Sanderson as follows: "when atoms initially different in electronegativity combine, they adjust to the same intermediate electronegativity in the compound" [22]. The main consequence is that both the electronegativity χ_X of a given atom X and its partial charge δ_X vary when this atom is chemically combined. These two parameters must be related. A linear relationship is usually assumed as follows:

$$\chi_X = \chi_X^0 + \eta_X \delta_X, \qquad (8)$$

where η_X is the hardness of atom X as introduced by Pearson. Hardness is related to the softness $\sigma_X = 1/\eta_X$ which provides a measure of the polarizability of the electronic cloud around X. Softness increases with the size of the electronic cloud, i.e. with the radius *r* of X. Therefore hardness varies as 1/*r*. According to the Allred–Rochow scale, electronegativity is proportional to Z_{eff}/r^2 [23].

Hardness may then be approximated as

$$\eta = k\sqrt{\chi^0}, \qquad (9)$$

where *k* is a constant that depends on the electronegativity scale, *k*=1.36 when Pauling electronegativ-

H 2,10 ;507																	He 3,20 ;411
Li 0,97 ;747	Be 1,57 ;587											B 2,02 ;517	C 2,50 ;465	N 3,07 ;420	O 3,50 ;393	F 4,10 ;363	Ne 5,10 ;326
Na 1,01 ;732	Mg 1,29 ;647											Al 1,47 ;606	Si 1,74 ;557	P 2,11 ;506	S 2,48 ;467	Cl 2,83 ;437	Ar 3,50 ;393
K 0,91 ;771	Ca 1,04 ;721	Sc 1,23 ;663	Ti 1,32 ;640	V 1,56 ;589	Cr 1,59 ;583	Mn 1,63 ;576	Fe 1,72 ;561	Co 1,75 ;556	Ni 1,80 ;548	Cu 1,75 ;556	Zn 1,66 ;571	Ga 1,82 ;545	Ge 2,00 ;520	As 2,20 ;496	Se 2,50 ;465	Br 2,69 ;448	Kr 3,10 ;418
Rb 0,89 ;779	Sr 0,99 ;739	Y 1,19 ;674	Zr 1,29 ;647	Nb 1,45 ;611	Mo 1,56 ;589	Tc 1,67 ;569	Ru 1,78 ;551	Rh 1,84 ;542	Pd 1,85 ;541	Ag 1,68 ;567	Cd 1,60 ;581	In 1,49 ;602	Sn 1,89 ;535	Sb 1,98 ;523	Te 2,15 ;501	I 2,33 ;482	Xe 2,60 ;456
Cs 0,87 ;788	Ba 0,97 ;747		Hf 1,36 ;631	Ta 1,50 ;600	W 1,59 ;583	Re 1,88 ;536	Os 1,99 ;521	Ir 2,05 ;514	Pt 2,00 ;520	Au 2,02 ;517	Hg 1,80 ;548	Tl 1,60 ;581	Pb 1,92 ;531	Bi 2,03 ;516	Po 2,12 ;505	At 2,28 ;487	Rn 2,30 ;485
Fr 0,86 ;793	Ra 0,95 ;754																

Fig. 11. Electronegativities χ_i and softness σ_i of atoms X_i.

ities are expressed in the frame of Allred–Rochow's model (Fig. 11).

The total charge z of a given chemical species is equal to the sum of the partial charges of all individual atoms $z = \sum -\delta_i$. This together with Eqs. (8) and (9) leads to the following expressions for:

$$\text{the mean electronegativity } \chi = \frac{\sum_i \sqrt{\chi_i^0} + 1.36z}{\sum_i 1/\sqrt{\chi_i^0}} \tag{10}$$

and

$$\text{the partial charge } \delta_1 = (\chi - \chi_l^0)/1.36\sqrt{\chi_i^0}. \tag{11}$$

Eq. (11) can also be written as

$$\delta_i = \sigma_i(\chi - \chi_i^0), \tag{12}$$

where

$$\sigma_i = \left(1.36\sqrt{\chi_i^0}\right)^{-1}. \tag{13}$$

The partial charge model provides an easy way to work out the mean electronegativity of chemical species and the charge distribution on each atom. In the case of the water molecule for instance Eqs. (3) and (5) lead to $\chi(H_2O)=2.49$, $\delta_H \approx +0.2$ and $\delta_O \approx -0.4$.

References

[1] J. Livage, M. Henry, C. Sanchez, Progr. Solid State Chem. 18 (1988) 259.

[2] J.P. Jolivet, de la solution à l'oxyde, InterEditions-CNRS, Paris, 1994.

[3] C.J. Brinker, G.W. Scherer, Sol–Gel Science, Academic Press, New York, 1989.

[4] C.F. Baes, R.E. Mesmer, Hydrolysis of Cations, Wiley, New York, 1976.

[5] C.K. Jorgensen, Inorganic Complexes, Academic Press, London, 1963.

[6] M. Henry, J.P. Jolivet, J. Livage, Structure and Bonding 77 (1992) 153.

[7] D.L. Kepert, The Early Transition Metals, Academic Press, London, 1972.

[8] M. Ardon, A. Bino, Structure and Bonding 65 (1987) 1.
[9] G. Fu, L.F. Nazar, Chem. Mater. 3 (1991) 602.
[10] G. Sposito, The Environmental Chemistry of Aluminium, CRC Press, Boca Raton, 1989.
[11] H. Stünzi, L. Spiccia, F.P. Rotzinger, W. Marty, Inorg. Chem. 28 (1989) 66.
[12] R.K. Iler, The Chemistry of Silica, Wiley, New York, 1979.
[13] R.M. Barrer, Hydrothermal Chemistry of Zeolites, Academic Press, London, 1982.
[14] M.T. Pope, Heteropoly and Isopolyoxometallates, Springer, Berlin, 1983.
[15] J. Livage, Chem. Mater. 3 (1991) 578.
[16] E. Matijevic, Ann. Rev. Mater. Sci. 15 (1985) 483.
[17] E. Matijevic, Acc. Chem. Res. 14 (1981) 22.
[18] A. Clearfield, P.A. Vaughan, Acta Cryst. 9 (1956) 555.
[19] A. Clearfield, Rev. Pure Appl. Chem. 14 (1964) 91.
[20] A. Clearfield, Inorganic Exchange Materials, CRC Press, Boca Raton, 1981.
[21] P. Bénard, M. Louer, D. Louer, J. Solid State Chem. 94 (1991) 27.
[22] R.T. Sanderson, Science 114 (1985) 670.
[23] A.L. Allred, E. Rochow, J. Inorg. Nucl. Chem. 5 (1958) 264.