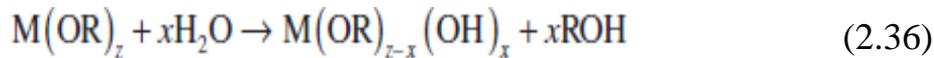


Procedures for Precipitation from Solution

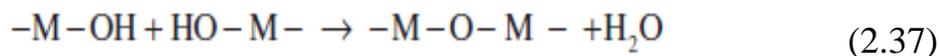
The most straightforward use of precipitation is for the preparation of simple oxides or hydrous oxides (also referred to as hydroxides or hydrated oxides). Precipitation is commonly achieved by hydrolysis reactions. Two main routes can be distinguished:

1. Hydrolysis of metal-organic compounds (e.g., metal alkoxides) in alcoholic solution, generally referred to as the *Stober process* and
2. Hydrolysis of aqueous solution of metal salts.

***Hydrolysis of Solutions of Metal Alkoxides:** Metal alkoxides have the general formula $M(OR)_z$, where z is an integer equal to the valence of the metal M , and R is an alkyl chain. They can be considered as derivatives of either an alcohol, ROH , in which the hydrogen is replaced by the metal M , or of a metal hydroxide, $M(OH)_z$, in which the hydrogen is replaced by an alkyl group. The reactions involve hydrolysis:



Followed by condensation and polymerization by dehydration:



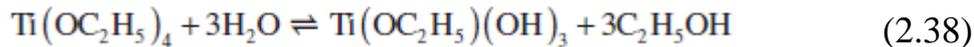
Stober et al. carried out a systematic study of the factors that control the preparation of fine, uniform SiO_2 particles by the hydrolysis of silicon alkoxides in the presence of NH_3 . The NH_3 served to produce pH values in the basic range.

For the hydrolysis of silicon tetraethoxide, $Si(OC_2H_5)_4$, referred to commonly as TEOS, with ethanol as the solvent, the particle size of the powder was dependent on the ratio of the concentration of H_2O to TEOS and on the concentration of NH_3 but not on the TEOS concentration (in the range of 0.02–0.50 mol/dm³). For a TEOS concentration of 0.28 mol/dm³, the particle sizes varied between 0.05 and 0.90 μm and were very uniform. Different alcoholic solvents or silicon alkoxides were also found to have an effect. The reaction rates were fastest with methanol and slowest with *n* butanol.

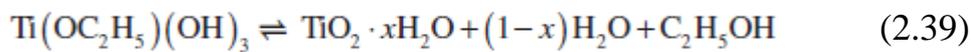
Likewise, under comparable conditions, the particle sizes were smallest in methanol and largest in *n*-butanol. Fastest reactions (less than 1 min) and

smallest sizes (less than 0.2 μm) were obtained with silicon tetramethoxide, while silicon tetrapentoxide reacted slowly (~ 24 h) and produced fairly large particles.

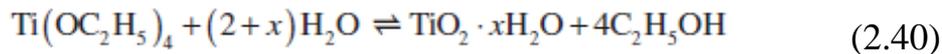
The controlled hydrolysis of metal alkoxides has since been used to prepare fine powders of several simple oxides. The alkoxides reacts with water to produce a monomeric hydrolysis species according to



However, the presence of dimers and trimers of the hydrolysis species cannot be excluded. Polymerization of the monomer to produce the hydrated oxide is represented by



The overall reaction can therefore be represented as



The value of x was found by thermo gravimetric analysis to be between 0.5 and 1. Most metal alkoxides hydrolyze readily in the presence of water, so that stringent conditions must be maintained to achieve powders with controlled characteristics. The reactions are sensitive to the concentration of the reactants, the pH, and the temperature. Oxide or hydrated oxide powders are produced.

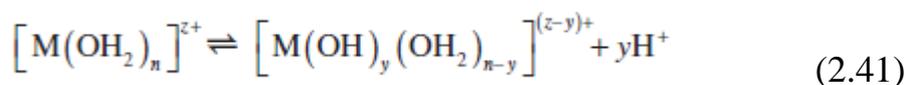
The precipitated particles are commonly amorphous and can be agglomerates of much finer particles (Fig. 2.9a).

Hydrolysis of Solutions of Metal Salts

Compared to the hydrolysis of metal alkoxides, the method has the ability for producing a wider range of chemical compositions, including oxides or hydrous oxides, sulfates, carbonates, phosphates, and sulfides. However, the number of experimental parameters that must be controlled to produce uniform particles is generally higher. They include the concentration of the metal salts, the chemical composition of the salts used as starting materials, the temperature, the pH of the solution, and the presence of anions and cations that form intermediate complexes. While a variety of particle sizes and shapes can be

produced, the morphology of the final particles can rarely be predicted. Furthermore, while amorphous as well as crystalline particles can be produced, the factors that determine the crystalline versus amorphous structure of the product are not clear.

Metal ions, as indicated earlier, are normally hydrated in aqueous solution. The conditions for homogeneous precipitation of uniform particles can be achieved by a *forced hydrolysis* technique. This technique is based on promoting the *deprotonation* of hydrated cations by heating the solution at elevated temperatures (90–100°C). For a metal M with a valence z , the reaction can be written



The soluble hydroxylated complexes produced by the hydrolysis reaction form the precursors to the nucleation of particles. They can be generated at the proper rate to achieve nucleation and growth of uniform particles by adjustment of the temperature and pH. In principle, it is only necessary to age the solutions at elevated temperatures. In practice, however, the process is very sensitive to minor changes in conditions. In addition, anions other than hydroxide ions play a decisive role in the reaction. Some anions are strongly coordinated to the metal ions and thus end up in the precipitated solid of fixed stoichiometric composition. In other cases, the anions can be readily removed from the product by leaching. Finally, in some case the anions affect the particle morphology without being incorporated in the precipitated solid. The specific conditions for the precipitation of uniform particles must therefore be adjusted from case to case.

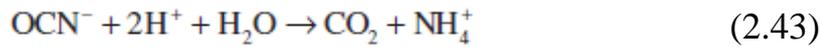
As an example of the sensitivity of the reactions to changes in conditions, we can consider the synthesis of spherical hydrated aluminum oxide particles with narrow size distribution). Solutions of $\text{Al}_2(\text{SO}_4)_3$, $\text{KAl}(\text{SO}_4)_2$, and a mixture of $\text{Al}(\text{NO}_3)_3$ and $\text{Al}_2(\text{SO}_4)_3$ or a mixture of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SO_4 were aged in Pyrex tubes sealed with Teflon lined caps at $98 \pm 2^\circ\text{C}$ for up to 84 h.

The conditions for nucleation and growth of uniform particles in solution can also be met by the slow release of anions from organic molecules such as urea or formamide. An example is the precipitation of yttrium basic carbonate particles from a solution of yttrium chloride, YCl_3 , and urea, $(NH_2)_2CO$.

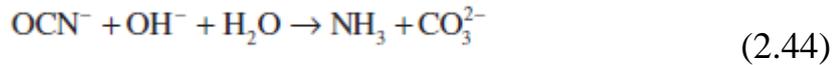
Particles of uniform size were produced by aging for 2.5 h at $90^\circ C$ a solution of $1.5 \cdot 10^{-2} \text{ mol/dm}^3$ YCl_3 and 0.5 mol/dm^3 urea. However, solutions of YCl_3 containing higher urea concentrations yielded, on aging at $115^\circ C$ for 18h, rodlike particles somewhat irregular in size. At temperatures up to $100^\circ C$, aqueous solutions of urea yield ammonium and cyanate ions:



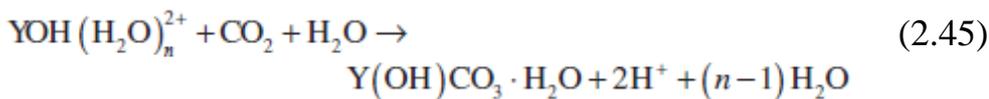
In acid solutions, cyanate ions react rapidly, according to



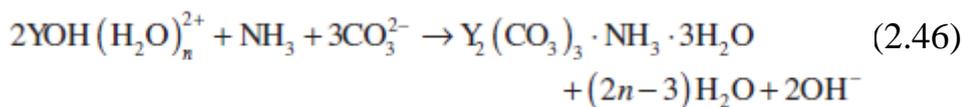
Where as in neutral and basic solutions, carbonate ions and ammonia are formed:



Yttrium ions are weakly hydrolyzed in water to $YOH(H_2O)_n^{2+}$. The resulting release of hydronium ions accelerates urea decomposition according to Eq. (2.43). The overall reaction for the precipitation of the basic carbonate can, therefore, be written as



For the reaction at $115^\circ C$, the decomposition of excess urea ($>2 \text{ mol/dm}^3$) generates a large amount of OH^- ions, which change the medium from acidic to basic (pH 9.7). The reaction of cyanate ions proceeds according to Eq. (2.45). The precipitation of rodlike particles may therefore be represented as:



In addition to an excess of urea and a higher aging temperature, longer reaction times ($>12 \text{ h}$) are needed to generate a sufficient amount of free ammonia for reaction Eq. (2.46) to dominate.