

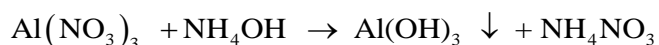
Lecture 6

Precipitation and co-precipitation

In this process, the desired component is precipitated from the solution. Co precipitation is used for simultaneous precipitation of more than one component. Catalysts based on more than one component can be prepared easily by co-precipitation. The precipitation process is used for preparation of bulk catalysts and support material such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 etc.

Process

In general, the metal hydroxides are precipitated from their precursor salt solution because of their low solubility. The precipitation of hydroxides can be performed either by starting from an alkaline solution which is acidified or from acidic solution by raising the pH. However, most hydroxides for technical application are precipitated from an acidic solution by the addition of an alkaline precipitating agent. Usually, ammonia or sodium bicarbonate is used as the precipitating agent. Highly soluble inorganic salts such as nitrates, carbonates or chlorides are generally used as metal precursors. For example, preparation of alumina is done by precipitating aluminium hydroxide from aluminium nitrate solution by addition of ammonium hydroxide.



During precipitation, several processes occur and the major steps are :

1. liquid mixing / supersaturation
2. nucleation
3. crystal growth to form primary products
4. aggregation of the primary particles

Initial mixing or interdispersing of components in the solution has a significant effect on the precipitation. Good mixing result in a more homogeneous product particularly in case of co- precipitation. Rate of stirring primarily affects the nucleation whereas growth rate is much less influenced by this factor. Stirring rate also affect the aggregation. Aggregate size can be influenced by changing the stirring rate and the manner of mixing.

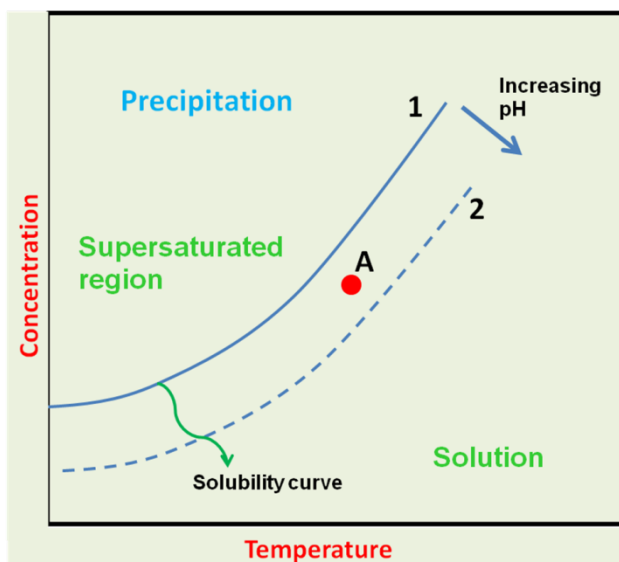


Fig 1. Parameters affecting supersaturation

For nucleation to occur the solution must be super saturated with respect to the components which is to be precipitated. Parameters affecting supersaturation is shown in Fig. 1. In supersaturated region the system is unstable and precipitation occurs with any small disturbance. The supersaturaton region is approached either by increasing the concentration through evaporation, lowering the temperature or by increasing pH. The solubility of a component increases with temperature as shown in Fig. 1. The solubility curve is also function of pH. As pH increases solubility decrease and curve shift from 1 to position 2. Then the point which was initially in solution region becomes in supersaturated region. The increase in pH is the most convenient method for precipitation. The reaction during precipitation, $M^{n+} + nOH^{-} \rightleftharpoons M(OH)_n$, is controlled by increasing the pH through addition of a basic solution. Hence by raising the pH value of a solution by addition of alkaline or ammonium hydroxide the corresponding metallic hydroxide compounds can be made insoluble and precipitated from solution. Commonly used

reagents are NaOH, KOH, NH₄OH, carbonates and bicarbonates. Particles within supersaturated region develop in two steps : nucleation and growth.

Nucleation may proceed spontaneously through the formation of M(OH)_n entities or be initiated with seed materials such as dust , particle fragments, roughness of vessels surface. Addition of seed material enhances rate of nucleation. The nucleus is defined as the smallest solid phase aggregate of atoms, molecule or ions which is formed during precipitation and which is capable of spontaneous growth. In super saturated solution when the concentration exceeds a critical threshold value, a nucleus will form and the precipitation will begin. As long as the concentration of the species stays above the nucleation threshold, new particles are formed. Nucleation starts with the formation of clusters which are capable of spontaneous growth by the subsequent addition of monomers until a critical size is reached. Clusters, smaller than the critical size, tend to re-dissolve, while larger clusters continue to grow. As soon as the concentration falls below the critical concentration due to consumption of the precursors by nucleation or by the growth process, only growth of existing particles continues. Growth proceed through adsorption of ions on surface of seeded particle. This growth is a function of concentration, temperature and pH. Rates of nucleation and growth can be independently controlled. If nucleation is faster than growth, the system produces a narrow distribution of small particles. Fast growth results in narrow distribution of large particles.

Several equations are proposed for nucleation rate and the most commonly used is :

$$\frac{dN}{dt} = \beta \exp \left[\frac{-16\pi\sigma^3 v^2}{3(kT)^3 \ln^2 s} \right]$$

where β is the pre-exponential term, σ is solid –fluid interfacial energy, v is solid molecular volume and T is the temperature. The super saturation ‘s’ is defined as the ratio of actual concentration to solubility; $s = \frac{\text{actual concentration}}{\text{solubility}}$

The equation can be simplified as $\frac{dN}{dt} = \beta \exp \left[\frac{-A}{\ln^2 s} \right]$ $A = \frac{16\pi\sigma^3 v^2}{3(kT)^3}$

Thus, nucleation strongly depends on the concentration as well as temperature. There is a critical super saturation concentration below which nucleation is very slow and above which nucleation is very fast.

There are several mechanisms of crystal growth and most of these lead to the simple equation of growth rate, $G = k(c - c_{eq})^n$, where 'k' is the kinetic coefficient, 'c' is the actual concentration and 'c_{eq}' is the equilibrium concentration. The value of exponent 'n' lies in the range of 1 to 2 and often close to 1.

Hence, the dependency of the crystallite growth rate on concentration is closer to a linear function while nucleation rate increases exponentially with concentration. Therefore, high super-saturation level promotes nucleation rather than crystal growth and favor the precipitation of highly dispersed materials. In contrast, precipitation from a more dilute solution tends to produce fewer but larger crystals.

Apart from nucleation and crystal growth, aggregation is also an important step. Aggregation leads to fewer and larger but yet porous particles. It is the formation of clusters of nano-scale primary particles into micrometer scale secondary particles. Physical and chemical forces can hold these particles together. Porosity is then determined by how the particles are stacked and the pores are considered as void spaces between the primary particles. Because of very high super-saturation during the precipitation of most base metal hydroxides or carbonates, nucleation is spontaneous.

Process variation

Precipitation process can be carried out in different ways. The process can be carried out either in batch mode or in continuous mode. The other process variation that affects the precipitate properties is the sequence of addition of the starting materials.

In a batch process, the salt solution from which the metal hydroxide is to be precipitated is taken in a vessel and the precipitating agent is added. The advantage of this method is its simplicity. However, variation of batch composition during precipitation process is a major limitation. This can lead to differences in the properties of the precipitate formed in the initial-and final stages. The continuous process involves