

**Advantages and disadvantages:** The main advantage of the precipitation process is the possibility of creating pure and homogenous material. However, the major disadvantages include necessity of product separation after precipitation and generation of the large volume of salt containing solutions. There is also difficulty in maintaining a constant product quality throughout the whole precipitation process if the precipitation is carried out discontinuously.

### Process parameters

In addition to the process variations discussed above there are many other parameters that affect the final product properties as shown in Fig.3. The properties of the final product that are affected include phase formation, chemical composition, purity, particle size, surface area, pore size and pore volume. It is necessary to optimize the parameters to produce the desired product.

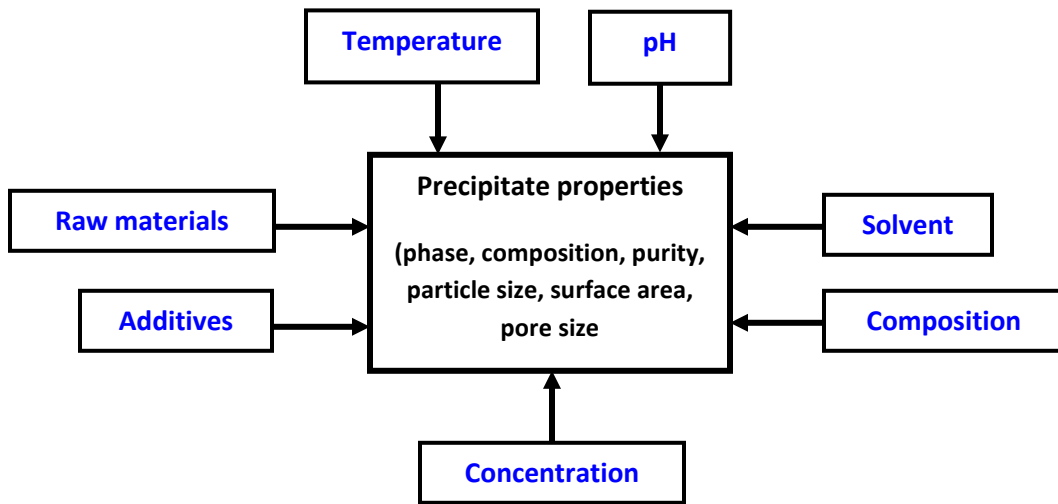


Fig. 3. Parameters affecting the properties of the precipitate

**Effect of raw materials :** The precursors are usually chosen with counter ions that can easily be decomposed to volatile products during heat treatment steps. Nitrates and carbonate salts are preferably used as metal precursors whereas ammonia or sodium carbonate as the precipitating agent. Chloride and sulphate ions act as poisons in many catalytic processes. Such ions should be avoided in the precipitation process. However, if the precipitation is needed to be carried out in the presence of these ions then repeated washing steps are necessary to remove these ions from the precipitate.

The nature of the counter ions present in the solution can also influence particle morphology, particle size and phase distribution. It has been observed that preparation of  $\text{MoO}_3$  from  $\text{Na}_2\text{MoO}_4$  precursor salt results in small particles with relatively high surface area whereas use of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  as precursor salt results in larger particles.

**Effect of pH :** pH directly control the degree of super saturation and hence is expected to affect the final properties. But the influence of pH is not simple and has to be investigated experimentally for the specific system. In aluminium oxide system, the precipitation pH is one of the parameters that determines the phase formation. In general, it has been found that precipitation in alkaline medium ( $\text{pH} > 8$ ) leads to the formation of bayerite ( $\beta\text{-Al}(\text{OH})_3$ ), while precipitation in more acidic conditions favors formation of boehmite ( $\gamma\text{-AlO}(\text{OH})$ ).

**Effect of concentration and composition:** It is desirable to precipitate at high concentration levels of metal ions. This increases the space time yields by decreasing the vessel volume for the same mass of precipitate. Moreover, higher degree of super-saturation leads to faster precipitation. Higher concentration levels also results in smaller particle size and higher surface areas due to increased nucleation rates.

If the catalysts are prepared by co-precipitation, the composition of solution determines the composition of the final product. Deviation from solution composition generally occurs if the solubilities of the different components differ significantly and the precipitation is not complete. The precipitation can be carried out simultaneously or sequentially. When the solubility of the components is not too different, then the precipitation will occur almost simultaneously. However, if the solubility of the components differs significantly then the component with lower solubility will preferentially precipitate resulting in sequential precipitation.

**Effect of solvent :** For preparation of bulk catalysts and supports, water is almost exclusively used as the solvent for economic reason. Organic solvents are much more expensive to use. Furthermore, solubilities of most metal salts used as the precursors are lower in organic solvents. Organic solvents are also environmentally hazardous. So use of organic solvents is very limited. These are used only in specific cases where product quality obtained is better by using organic solvent.

**Effect of temperature :** The precipitation temperature is a decisive factor in controlling precipitate properties such as primary crystallite size , surface area and the phase formed. Till date it is very difficult to predict the exact nature and extent of effect of the precipitation temperature on the properties and is generally determined experimentally. Nucleation rates are extremely sensitive to temperature. In general, most precipitation processes are carried out above room temperature , often close to 373 K for obvious reason that the precipitation is more rapid. A higher temperature may result in an increase in crystallite size, though this depends on the kinetics of different elementary processes. Sometimes, no effect of temperature or even lowering of size of the crystallites is observed as in the case of ZnO system. Temperature also affects the phase formation. During preparation of Ni/SiO<sub>2</sub> catalysts, at high temperatures nickel hydro-silicate is obtained while at lower temperatures, the main precipitate is nickel hydroxide.

When use of high temperature is detrimental, the rotary evaporator is often used to remove the solvent from slurry solution. Rotary evaporator is a vacuum evaporator in which pressure is lowered above the slurry so that boiling point of the solvent is reduced and it can be removed without using excessive heating. In the evaporator a rotating evaporating flask is connected to vapor duct to draw off the vapor and thereby, reduce the pressure within evaporator system. Sample solution is gently heated in bath, usually water bath, to enhance the solvent removal. The separated solvent vapor can be condensed back using a condenser and collected in a separate flask.

**Effect of Additives :** Additives are substances which are not necessary ingredients of a precipitation reaction. The properties of the precipitates can strongly be influenced by additives. The most widely used additives are organic molecules which are added to the precipitate in order to control the pore structure. Such organic molecules can later be removed from the precipitate in the calcination step.

A very promising route for the preparation of the high surface area oxides is the use of surfactants as additives. Removal of the surfactant by calcination steps leaves a well-defined pore network. The pore diameter can be adjusted in the range of 2-10 nm. These all are treated as trade secrets and details are not available in the public domain.

### **Preparation of dual oxides catalysts by coprecipitation**

Mixed oxide support and catalyst can be prepared by coprecipitation method. As discussed earlier, for coprecipitation, the solubility of the two components should be in similar range for simultaneous precipitation resulting in homogeneous product. Otherwise the precipitation will be sequential resulting in non-homogeneous product.

Two examples are discussed below.

#### **1. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>**

SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is used in catalytic cracking process and is also used as support for active metals in various applications. Preparation of dual oxides by coprecipitation is similar to precipitation of single oxide. At pH 6 (at 50 °C) the precipitation of both silica and alumina sols begins and gelation takes places.

#### **2. NiO-Al<sub>2</sub>O<sub>3</sub>**

NiO-Al<sub>2</sub>O<sub>3</sub> is used for hydrogenation and methanation reactions. Although this catalyst can be produced by other route, coprecipitation method of preparation is also done to increase the intimate interaction between active metal and support. The sodium bicarbonate can be used as precipitating agent for formation of nickel aluminium hydroxyl carbonate with good homogeneity of final product.