Lecture 9

Washing and filtering

Washing can be done by decantation. This method is time consuming. In this method the precipitate or gel is added to a large volume of distilled water and the suspension is thoroughly stirred. Then, the suspension is allowed to settle. The foreign undesirable ions are desorbed from particles as they settle down slowly at the bottom. When a clear interface is visible, the water is removed by decantation and the process is repeated. The number of washings required is determined by checking the impurity level of the decanted water. After washing, the precipitate or gel is filtered. The process can be reversed. That is the filtration is done first and the precipitate or gel is washed with distilled water in the subsequent step. This method takes less time. Impurity level in the wash water is checked to determine the required number of washings.

Drying

Drying is described as the elimination of water or solvent from the pores of the precipitate or gel. It can be done in two ways:

- Solvent evaporation
- Super critical drying

Solvent evaporation : This type of drying is done in a conventional oven at 100-200 ^{0}C and is generally accompanied by a contraction of the structure. In case of gel, the product obtained from ordinary drying is known as dry gel or xerogel. Initially, drying occurs through evaporation of moisture from the outside surface of the materials. The rate of water loss is constant and the mass transfer is controlled by temperature, relative humidity and flow rate of air over the surface and the size of the filtrate. The process continues until the moisture content drops to about 50%. Continued moisture loss occurs with a declining rate in which evaporation is controlled by capillary forces. The saturation point decreases as the pore become smaller and the evaporation slows until water is forced into larger pores by concentration gradient. At the moment of drying, as the pore liquid is evaporated from a gel network, the capillary pressure associated with the liquid vapor interface within a pore can become very large for small pores. The capillary pressure that can develop in a pore of

radius r is $P = \frac{2\gamma\cos\alpha}{r}$, where P is capillary pressure, γ is surface tension, r the pore radius and α is the contact angle between liquid and solid. The capillary pressure with water evaporating from a pore with a radius of 1 nm is in the order of 1480 atm. Large capillary tension can lead to collapse of internal structure resulting in loss of pore volume and surface area. This phenomenon is more significant for a gel having more intricate porous structure compared to ordinary precipitated material. For a given pore size, the capillary pressure can be reduced by

1. Using a solvent with a lower surface tension or with a contact angle close to 90^0.
2. Eliminating the liquid -vapor interface altogether with either supercritical or freeze drying.

If temperature gradient is high so that evaporation rate is much faster compared to removal of moisture that is slowed by smaller pores, then large internal pressure of steam develops and also leads to collapse of structure. Therefore, high temperature gradient in the sample must be avoided. Drying at a lower temperature gives less surface area loss since evaporation rates are lower.

<u>Supercritical drying</u> is aimed at eliminating the liquid vapor interface and the accompanying capillary pressure responsible for structure collapse during conventional drying particularly for gels. It is used where retention of original microstructure of the product is important. This process typically involves displacement of water using an alcohol followed by removal of this alcohol/water mixture using supercritical carbon dioxide. In this process, the gels are placed in an autoclave filled with ethanol. The system is pressurized to at least 750-850 psi with CO_2 and cooled to 5-10 ^{0}C. Liquid CO_2 is then flushed through the vessel until all the ethanol has been removed from the vessel and gels. When the gels are ethanol-free, the vessel is heated to a temperature above the critical temperature of CO_2 (31 ^{0}C). As the vessel is heated, the pressure of the system rises. CO_2 is carefully released to maintain a pressure slightly above the critical pressure of CO_2 (1050 psi). The system is held at these conditions for a short time, followed by a slow, controlled release of CO_2 to ambient pressure. As with previous steps, the length of

time required for this process is dependent on the thickness of the gels. The process may last anywhere from 12 hours to 6 days.

Calcination or sintering

After the removal of pore liquid, further heat treatment is necessary to convert the precipitate or dry gel to catalytically useful form. After drying, the next step of heat treatment is known as calcination. Often the heating is done in the presence of flowing air or oxygen to burn any residual organics or to oxidize the sample. Multiple changes occur during this process including:

1. Active phase generation: The hydroxide form is converted to oxide form.

2. Stabilization of mechanical properties: The catalysts sample is subjected to a more severe heat treatment than that is likely to be encountered in a reactor. This ensures the stability of its textural and structural properties during reaction.

3. Loss of chemically bound water: The chemically bound water is removed at higher temperature.

4. Changes in pore size distribution and surface area due to sintering: Exposing the sample to high temperature over an extended period of time leads to sintering and consequently decreases the surface area.

5. Change in phase distribution: Higher temperature cause material to crystallize into different structural forms. Fig. 1 shows the formation of various phases of alumina when calcined at different temperatures.

The extent of change in the physical characteristics of the final sample depends on following parameters: temperature, heating rate, heating time and gaseous environment.

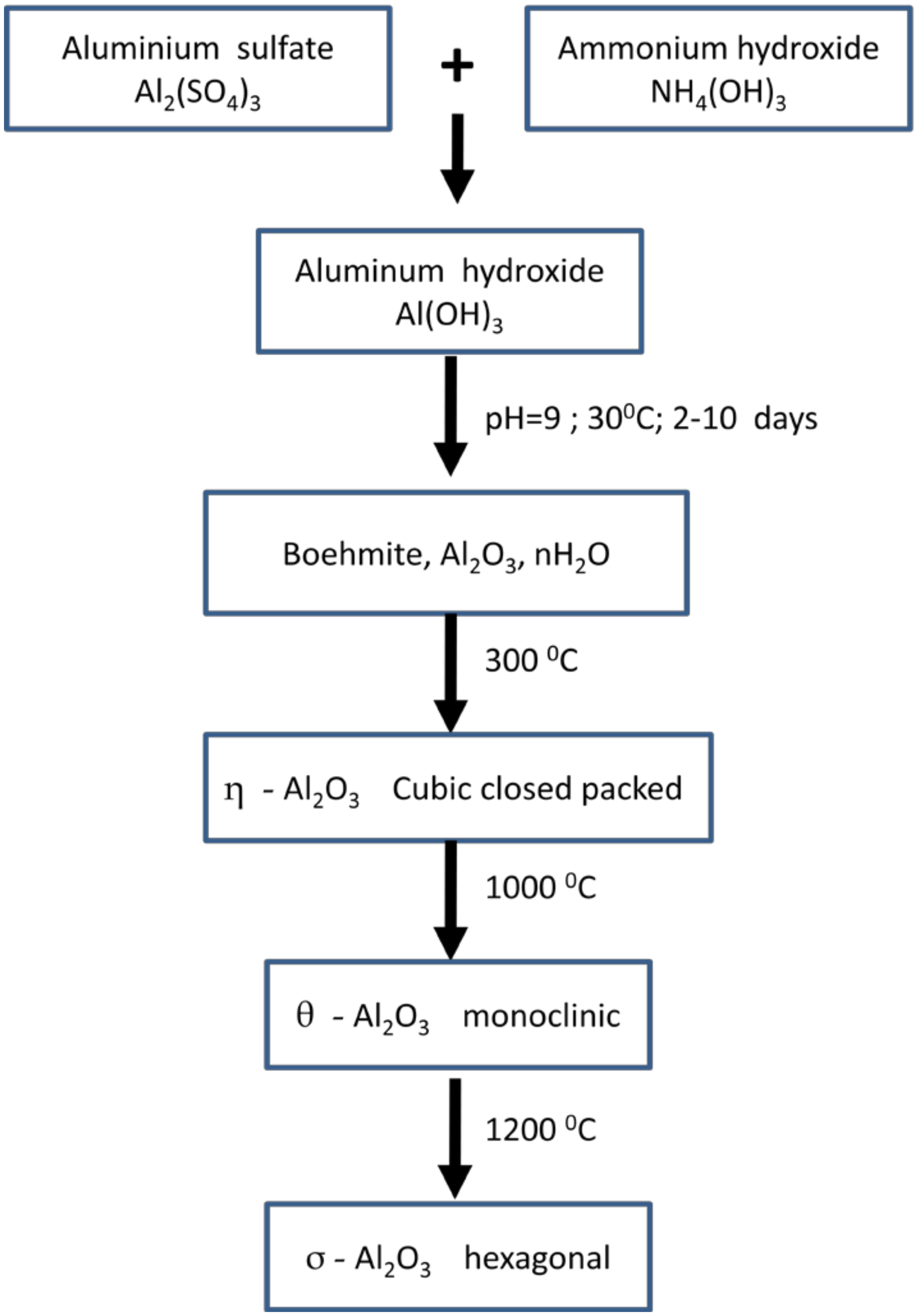

Fig. 1. Formation of various phases of alumina on calcination at different temperatures