

Chapter Seven

CONCLUSIONS

The present investigation deals with the systematic study of equilibrium dehydration-rehydration behavior followed by kinetics of thermal dehydration and dehydroxylation process of two different types of high alumina bearing materials such as naturally occurring bauxite rock and synthetically prepared alumina hydrate based on their thermogravimetric(TG) and differential thermogravimetric (DTG) analyses respectively under both the isothermal and non-isothermal conditions. Novel efforts have also been adopted to elucidate the exact mechanism of thermal decomposition steps for two types alumina materials using updated dynamic kinetic models.

Bauxite rock, very rich in alumina, is a solid solution of a number of hydrated alumina phases containing varying proportions of gibbsite, boehmite and diaspore etc. Similarly, synthetically prepared alumina hydrate by wet chemical route vary to a great extent in respect of proportion of alumina phases present, degree of crystallinity, specific surface area, nature of bonding of water molecules depending on the preparatory conditions. However, water molecule is an integral part of all the hydrated layer lattice aluminous materials in which bauxite and synthetic alumina hydrates belonging to. The water molecules are constitutionally bonded to the structure of monohydrated or trihydrated alumina phases. Al_2O_3 is the major constituent of all aluminous materials.

Dehydration starts with the loss of physically adsorbed water, interlayer water followed by the loss of hydroxyl groups from their structure which is basically a heterogeneous solid state reaction and mainly governed by the rate of diffusion of formed water molecules through the structure.

For the purpose of thermal study, raw bauxite of Sourashtra, Gujrat, India predominantly gibbsitic in nature along with a synthetically prepared boehmitic alumina hydrate were chosen. They were thoroughly characterized by chemical analysis, specific surface area, FTIR spectroscopy, DTA, XRD and SEM studies.

The hydrated aluminous materials assumed more than 25 polymorphic phases with gradual expulsion of water molecules upon progressive heat treatment to higher temperature by which it undergoes progressive variations of crystallography, specific surface area, grain morphology until most stable form of alumina, corundum is obtained.

A comprehensive thermal dehydration-rehydration characteristic of bauxite rock and synthetic alumina hydrate in powder form in relation to variation of temperature of heat treatment and relative humidities of environment were carried out. The bauxite as well as synthetic alumina hydrate exhibited high surface activity at 300°C in all humidities, although synthetic alumina hydrate had much higher quantum of surface active behavior. Hence, synthetic alumina possessed more reversibility on rehydration than the bauxite. However, both the aluminous materials became more or less surface inactive at and above 800°C particularly at lower humidities of environment.

Kinetics of thermal decomposition for such two different types of hydrated aluminous materials under isothermal condition was interpreted and correlated from their thermogravimetric data with the help of ICTAC recommended integral isoconversional method and well acclaimed Guggenheim method. The important kinetic parameters such as rate constants, extent of validity of 1st order law and activation energies at initial and final stages of dehydration of both the samples were

evaluated. TG-DTA curves of gibbsitic bauxite and synthetic alumina hydrate samples revealed that thermal decomposition occurs via two well defined steps in both cases. However, in case of synthetic alumina hydrate decomposition starts at much lower temperature.

The activation energies estimated for initial stage and final stage of thermal dehydration (1st step) by Guggenheim method ($56.06 \text{ kJ.mole}^{-1}$) is consistent with that (48 kJ.mole^{-1}) by the ICTAC recommended method.

Furthermore, activation energy required for the final stage of dehydration (16 kJ.mole^{-1}) is always lower than that of initial stage of dehydration. The effect in particle size fraction on the kinetics of thermal decomposition of aluminous materials appears negligible.

Applying isoconversional FWO, model free Kissinger and modified Coats-Redfern models on the DTG data of respective aluminous materials at three different heating rates. Average activation energy computed for the 1st step and 2nd step of thermal decomposition of respective sample was observed to be well consistent with one another and also with values from other reference sources. Malek method showed that thermal decomposition process of bauxite is governed by a contracting area (R2) which in case of synthetic alumina hydrate contracting volume (R3) kinetic model is followed.

The kinetics parameters obtained under isothermal and non-isothermal condition were precisely analyzed, compared and optimized to find out best fitting models. The kinetic equation governing the thermal decomposition reaction of two types of alumina bearing materials were also computed.

The application of non-isothermal kinetic methods for determining the activation energy, pre-exponential factor and decomposition mechanism for initial dehydration step or later step for expulsion of hydroxyl group for the hydrated aluminous material using respective TG-DTGA data approaches closely to the practical conditions prevailing on their thermal decomposition process which duly considers the heating rate and degree of dissociation as the important variables.

The kinetic parameters derived for thermal decomposition of hydrated alumina materials via the isothermal and non-isothermal models differ widely because of certain limitations, assumptions and simplifications adopted in isothermal approach. In addition, a large volume data handling makes the calculation and drawing of curves very difficult, cumbersome and not totally errorless.

The slight variation in results based on same DTG data using different heating rates given hydrated alumina sample may be attributed to certain approximation made with a particular model, although all the three models are found to yield satisfactory and comparable values of kinetic parameters which holds good for decomposition kinetics of hydrated aluminous materials.

In conclusion, non-isothermal approach is the accurate, valid and better option in determining the thermal decomposition kinetics of hydrated aluminous materials rather than hypothetical isothermal way.

Therefore from technological point of view, the evaluation of different kinetic parameters by applying the non-isothermal kinetic models will provide accurate data on thermal decomposition of aluminous minerals in terms of energy consumption, nature of product derived and degree of reversibility which can be successfully utilized for proper calcination process of high aluminous materials in efficient manner.