Study on the Thermal Properties of Some Inorganically Modified Pre- Baked Clay Samples

IMTIAZ AHMAD*, MOHAMMAD. SHAKIRULLAH, M.ISHAQ, IMDAD ULLAH MOHAMMADZAI AND HAMEED ULLAH
[1]*Institute of Chemical Sciences, University of Peshawar, Pakistan.*
patwar2001@yahoo.co.in*

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Summary: The paper is focused on the influence of some inorganic modifiers on the thermal stability of the clay-inorganic intercalates. The inorganic modifiers used were NaOH and KOH. Solvent intercalation procedure was used. Clay was modified at 150, 500 and 750 ^{o}C, separately with NaOH and KOH. TGDTA study was performed to evaluate the thermal stability of the resultant intercalates. Intercalation with NaOH and KOH performed at 150 ^{o}C showed significant mass loss. Intercalation with NaOH performed at 500 and 750 ^{o}C, separately showed less mass loss compared to the ones prepared at 150 C^{o}. and hence exhibited thermal stability. In case of intercalation performed with KOH at 500 and 750 C^{o}, separately, the mass loss was comparable to the original pre-baked clay.

Introduction

Clay and clay intercalates are the focus of research due to their superior thermal, chemical, sportive and catalytic properties. Thermal stability is desired in certain applications particularly when clay is used as catalyst carrier, catalyst itself, molecular sieve or as adsorbent. Exposure to heat can cause sintering, exfoliation, agglomeration, and cementation, hence leading to loss of surface and porosity rendering clay unsuitable to be used in specific applications. In order to retain integrity of clay, there is a need to modify it with some inorganic compounds and to impart it certain superior properties.

Clay modification was studied to enhance their adsorptive capabilities [1-5]. Clay modification with some inorganic compounds to get the resultant product having superior properties have also been reported elsewhere [6-10]. However, the shortcomings of clay modification are the loss of surface area and porosity due to insertion of modifiers in to the interlayer spacing and galleries [11, 12]. As it is well established that the properties of intercalates depend on the nature of the clay, the type of chemical intercalates and the synthesis conditions [13-15], hence, selection of starting clay would certainly effect the resultant intercalates.

We report on the modification of pre-baked clay with sodium and potassium hydroxides at 150 , 500 and 700 ^{o}C to get thermally stable intercalates.

Results and Discussion

Clay has got tremendous attention of researchers due to its application at higher temperature. For this purpose, the clay must be thermally stable. In order to study, the effect of intercalations performed in current investigation on the thermal properties; the original and modified clay samples were analyzed using thermo gravimetric and differential thermal analyzer. The chemical composition of the original pre-baked clay sample is reported elsewhere [16].

The TG-DTA curves obtained in case of original as well as clay-NaOH and clay-KOH intercalates heated at 150, 500 and 750 ^{o}C, are provided in Figs. 1-7.

TG curves obtained for original clay and clay samples modified with NaOH and KOH are provided in Figs. 1-3. For original sample, the mass loss was found to be 0.079 mg when heating clay from 0 ^{o}C to 150 ^{o}C during the development of the thermo gram. For sample treated with NaOH and KOH and previously heated at 150 ^{o}C, the mass losses observed were 0.194 mg, and 0.321 mg, respectively. It is observed that the mass loss in case of original sample is less than the mass losses observed in case of intercalates prepared at 150 ^{o}C. The mass loss observed in case of original clay is due to the release of physio sorbed and free water, known as zeolitic water [17, 18]. The mass loss observed in case of both intercalates is quite significant. This can be due to expulsion of imbibed water mostly caged with in the pores. As during intercalation, Na and K get drilled in to the matrix leading to generation of more surface area which enhance the heat flow through the pores leading to exile of water caged in the pores. TG curves of clay sample intercalated at 500 ^{o}C with NaOH and KOH are provided in Figs. 4-5. Mass loss observed in case of original clay is 0.193

*To whom all correspondence should be addressed.

mg. Mass loss can be observed at 150 and 500 ^{o}C regions in the thermo gram. The mass loss observed at 150 ^{o}C is 0.160 mg, and at 500 ^{o}C is 0.081 mg in case of NaOH intercalated sample. Upon comparing with the mass loss of original clay (0.193 mg), the mass loss observed in case of intercalate prepared at 500 ^{o}C is quite low (0.081 mg). In case of KOH intercalated sample, the mass losses noted in the two regions of the thermogram are 0.081 mg, 0.182 mg, respectively. The mass loss observed at 500 ^{o}C region of the chromatogram is comparable with the original clay sample. Thus, it is inferred from the results that intercalates resulted from clay treated with NaOH gained thermal stability. However, in case of intercalate previously heated with KOH at 500 ^{o}C, the thermal stability is comparable with the original clay.

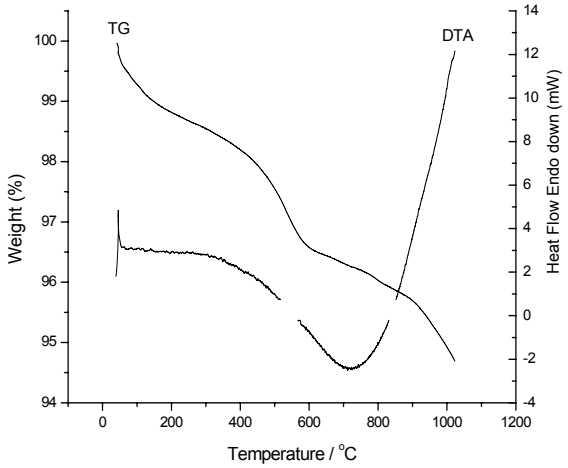

Fig. 1: TG-DTA curves of virgin clay sample

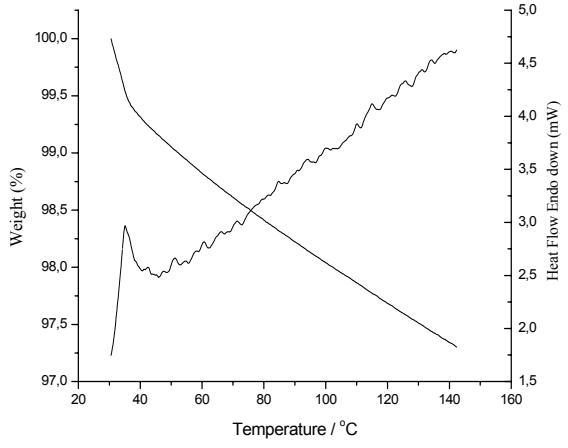

Fig. 2: TG-DTA curves of clay sample modified with NaOH at 150 ^{o}C

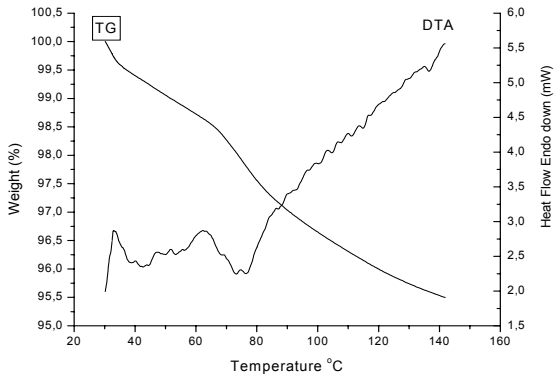

Fig. 3: TG-DTA curves of clay sample modified with KOH at 150 ^{o}C

TG curves of clay samples intercalated with NaOH and KOH at 750 ^{o}C are provided in Figs 6-7. A mass loss at 150, 500 and 750 ^{o}C regions of the thermogram could be observed. The mass losses are 0.0001 mg, 0.027 mg, and 0.002 mg, respectively. The mass loss observed at 150 ^{o}C is quite lower than the original sample. Similarly, the mass losses in case of intercalates observed at 500 and 750 ^{o}C are also quit lower than the mass losses observed in case of original clay. It is concluded from the thermograms that the sample intercalated at 500, and 750 ^{o}C with both NaOH and KOH shows less mass loss compared to intercalates prepared at 150 ^{o}C.

DTA curves are also provided in Figs. 1-7. Fig. 1 shows an endothermic peak in the temperature range of 400-800 ^{o}C with a distinct shoulder towards low temperature side and a large exothermic peak beyond 800 ^{o}C could also be observed. The endothermic peak is originating due to the imbibed or adsorbed water [19, 20]. The exothermic peak is indicative of some decomposition reactions releasing heat [21-24].

Figs. 2 and 3 show the DTA curves of the clay-NaOH and clay-KOH intercalates preheated at 150 ^{o}C. Fig. 2 shows the DTA curve of clay-NaOH intercalate preheated at 150 ^{o}C. A very small exothermic hump is observed at 30-35 ^{o}C. This is due to exothermic reaction of sodium hydroxide with the adsorbed water. From 35 -50 ^{o}C, an endothermic peak with a very small valley is observed. This is due to evolution of water which is present in very small amount compared to the original clay sample. As the sample was preheated with NaOH at 150 ^{o}C, hence most of the adsorbed water was expelled giving a very small endothermic peak. The DTA curve also features an exothermic curve in the temperature range 50-150 ^{o}C. This is due to some decomposition

reactions [25]. Fig. 3 shows the DTA curve of clay-KOH intercalate preheated at 150 ^{o}C. The curve shows similarity with the one depicted in Fig. 2. The same explanation can be thought for both endothermic and exothermic peaks.

Figs. 4 and 5 show the DTA curves of the clay-NaOH and clay-KOH intercalates preheated at 500 ^{o}C. Both the thermo grams are identical showing an initial very small endothermic hump at temperature below 50 ^{o}C. In case of clay-NaOH intercalate, another small hump is seen at 200-250 ^{o}C. This peak is absent in case of clay-KOH intercalate. This is due to extrusion of chemisorbed water. Beyond 250 ^{o}C, very pronounced exothermic peaks are originating in both the curves till 500 ^{o}C. These exothermic peaks are diagnostic of decomposition reactions.

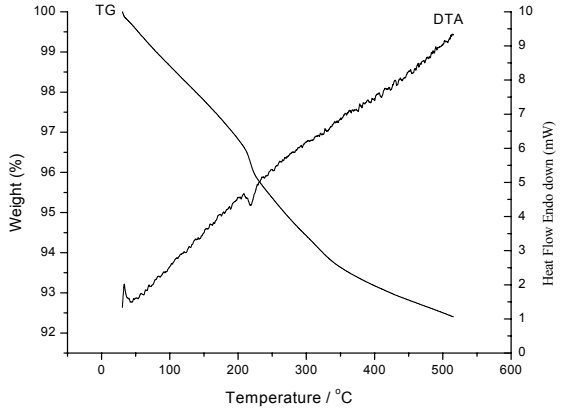

Fig. 4: TG-DTA curves of clay sample modified with NaOH at 500 ^{o} C

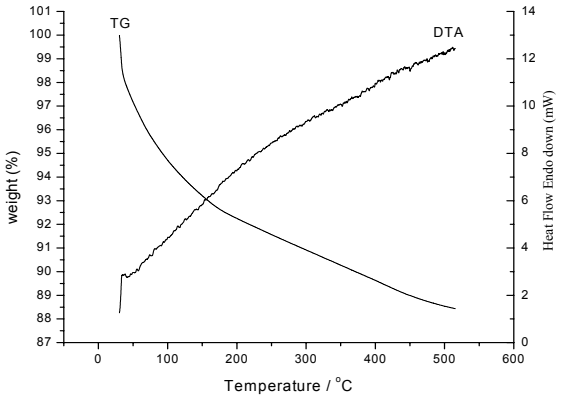

Fig. 5: TG-DTA curves of clay sample modified with KOH at 500 ^{o} C

The DTA curves of clay-NaOH and clay-KOH intercalate preheated at 750 ^{o}C are provided in Figs. 6 and 7.In case of both samples, endothermic peaks are originating in the temperature range of 50-250 ^{o}C. Beyond 250 ^{o}C, exothermic peaks are originating till 750 ^{o}C. The shape of DTA curves indicates the loss of water in the temperature range of 50-250 ^{o}C and decomposition reactions in the temperature rang of 250-750 ^{o}C.

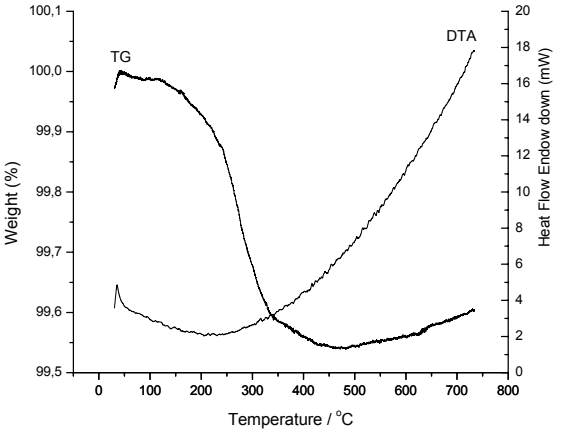

Fig. 6: TG-DTA curves of clay sample modified with NaOH at 750 ^{o} C

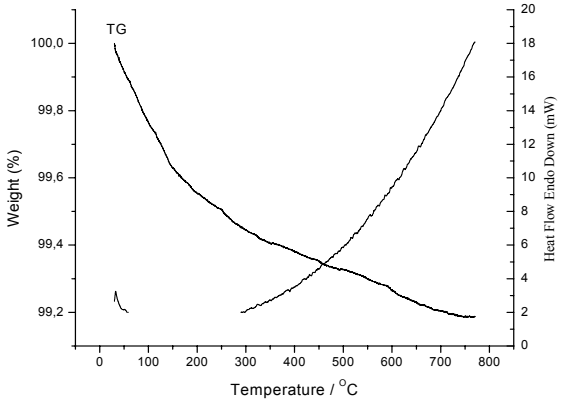

Fig. 7: TG -DTA curves of clay sample modified with KOH at 750 ^{o} C

It is inferred from the results that the endothermic and exothermic curves in case of virgin and various modified clay samples are appearing at different temperatures. In case of original clay sample, the endothermic peak appears at about 400 ^{o}C. In case of modified samples, the curves are appearing at 50 ^{o}C. However, in case of samples modified with NaOH and KOH and preheated at 150 ^{o}C, a small exothermic peak precedes the endothermic peak. Similarly, the endothermic peaks originating in the samples preheated with NaOH and KOH at 500 ^{o}C are very small. These peaks are quite distinct in case of preheating the clay with NaOH and KOH at 750 ^{o}C which start appearing at 50-250 ^{o}C compared to the original clay where the endothermic

peak is appearing at 400 ^{o}C. It is inferred from the results that the insertion/intercalation of both NaOH and KOH has changed the behavior of DTA curves. The reason can be thought is the hydrolysability of Na and K. Water molecules accumulate around the Na and K in the intercalates and get physiosorbed. For its extrusion, heat is required thus giving endothermic curves in the low temperature range compared to the original clay. Amongst the intercalates, the ones preheated at 750 ^{o}C giving pronounced endothermic peaks at low temperature range compared to the intercalates preheated at 150 and 500 ^{o}C, which give peaks with poor intensity. It is inferred from the results that intercalates prepared at 750 ^{o}C are more hydrolysable compared to the ones preheated at 150 ^{o}C and 500 ^{o}C with NaOH and KOH, separately. From the TG and DTA curves, it can be seen that the intercalates prepared at 500 ^{o}C contain fewer adsorbed/chemisorbed water and can with stand heating with out significant mass loss compared to intercalates preheated at 150 and 750 ^{o}C.

Experimental

Collection of Sample

A pre-baked clay sample was collected from brick kiln, ground, and dried in an oven at 105 ^{o}C in order to remove the surface moisture.

Solvent Intercalation

The clay sample was intercalated in a vat with NaOH and KOH, separately while varying the temperature. For evaluating the temperature influence on the thermal stability of the resultant intercalates, one gm portions of pre- baked clay sample were subjected separately to solvent interaction using NaOH and KOH (1 %) as intercalating agents. 10 ml aliquot of the respective solution was added to each sample and the resultant past was heated at 150, 500 and 750 ^{o}C in a muffle furnace. Each of the resultant intercalates was washed with copious amount of de-ionized water, dried in a vacuum oven in order to remove all the surface and entrapped moisture. The prepared samples were kept in vials for thermal studies.

Thermogravemetric and Differential Thermal Analysis

For thermogravemetric analysis, the samples were analyzed using Thermogravemetric and Differential Thermal Analyzer (TGDTA) to decide about mass loss in a particular temperature range and to evaluate their thermal resistance.

Conclusion

It is inferred from the TG results that intercalates obtained at 150 ^{o}C did not attain significant improvements in thermal stability. Intercalates prepared at 500 ^{o}C showed thermal stability. The mass loss in case of intercalates prepared at 750 ^{o}C is comparable with the original clay. The DTA study also confirm that the intercalates prepared at 500 ^{o}C were lean in chemisorbed water compared to intercalates prepared at 150 and 750 ^{o}C as evident form the endothermic and exotermic peaks. The effect of NaOH and KOH was also studied. It is inferred from the results that intercalates resulted from clay treated with NaOH at 500 ^{o}C gained thermal stability. However, in case of intercalate previously heated with KOH at 500 ^{o}C, the thermal stability is comparable with the original clay.

Acknowledgement

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