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Thermal characterization of ammonium alum

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Abstract Thermal decomposition of ammonium alum was studied by simultaneous thermogravimetry (TG)-differential scanning calorimetry (DSC) attached to a Fourier transform infrared (FTIR) spectrometer, so that each mass loss was related with the simultaneous endo- or exothermal behavior and to the FTIR absorption produced by the evolved gases. Apart from some clear dehydration and desulfation processes, other overlapping peaks were observed by DSC, TG, and FTIR. Optimal fitting to logistic mixture models was performed to separate the overlapping processes. Deconvolution of overlapping DTG peaks resulted in single constituent peaks, which were related to plots of some specific FTIR bands along time. Thus, a more accurate insight of the chemical processes taking place was obtained.

Keywords Alum · TG · DSC · Logistic mixture

Introduction

Ammonium alum is used in tanning, in dyeing and fireproofing textiles, in vegetable glues and porcelain cements, and in water purification [1]. It is also used in cosmetic formulations such as cleansing products, skin care products, moisturizers, face powders, and deodorants. Ammonium alum is a common ingredient in animal repellent sprays [2–4], fertilizer, and food preservatives. Chemically, it is hydrated ammonium aluminum sulfate, with the formula $(NH_4)Al(SO_4)_2{\cdot}12H_2O$. It occurs naturally as the rare mineral tschermigite [5]. Thermogravimetry (TG) has been used to investigate thermal decomposition of alums and related compounds [6–8]. Nevertheless, in the case of ammonium alum, some of the decomposition processes are still not clear. In this study, a synthetic hydrated potassium aluminum sulfate is investigated by simultaneous TG-differential scanning calorimetry (DSC), attached to a Fourier transform infrared (FTIR) spectrometer. The gases evolved from the alum decomposition are continuously analyzed by FTIR to identify some of the decomposition products. In addition, the TG curve will be fitted to a mixture of logistic functions to separate overlapping processes [9–12].

Experimental

The material, synthesized at Universidad de Málaga, consisted of a white powder. It was dried at 60 °C and then let to equilibrate at room temperature in open cups.

The original sample was analyzed by XRD to verify its crystalline structure. Cu Kα radiation (1.540596 and 1,544493 Å) was used on a Siemens D5000 diffractometer operated at 40 kV and 30 mA with Bragg–Brentano geometry. The 2θ angle was settled between 10 and 80°. Diffract V.8.0 Bruker-AXS software was used to evaluate the resulting diffractogram.

A part of the material was preheated for 24 h at 100 °C.

Both fresh and annealed samples were subjected to simultaneous TG/DSC analysis in a TA Instruments SDT

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2960. A 20 °C/min heating ramp was applied up to 1100 °C, with air flow at 50 mL/min. Samples of about 20 mg were placed in open alumina pans. The gases evolved from the SDT were continuously analyzed in a Bruker Vector 22 controlled through the Bruker Opus software.

Results

Figure 1 shows the XRD diffractogram obtained from the synthesized material. Aluminum ammonium sulfate hydrate [$(NH_4)Al(SO_4)_2(H_2O)_{12}$] was the only crystalline phase identified in the sample.

Figure 2 plots the TG, DSC, and DTG curves obtained from the fresh and the preheated samples. The alum degradation can be divided into three steps. The first step, between room temperature and 300 °C, is related to dehydration. The corresponding chemical reaction is

$$\left[(NH_4)Al(SO_4)_2(H_2O)_{12}\right] \rightarrow \left[(NH_4)Al(SO_4)_2\right] + 12\ H_2O$$

The theoretical mass loss has been calculated taking into account the stoichiometry, and should represent 47.7% of the initial mass. This result agrees with that measured from the aforementioned first step of the TG curve (47.8%).

Figure 3 shows an overlay of the TG and DTG curves and the FTIR spectra obtained from the gases evolved during the experiment with the fresh sample. The second step, between 450 and 600 °C, is related to sulfate decomposition process, which was evidenced by FTIR ammonia detection in the evolved gases. The process can be described by the following expression:

$$2\left[(NH_4)Al(SO_4)_2\right] \rightarrow 2\ NH_3 + (SO_4)_3Al_2 + SO_2 + H_2O + 0.5\ O_2$$

The mass loss measured on the TG curve was 14.3%, which agrees considerably well with the 14.6% value calculated from the reaction stoichiometry.

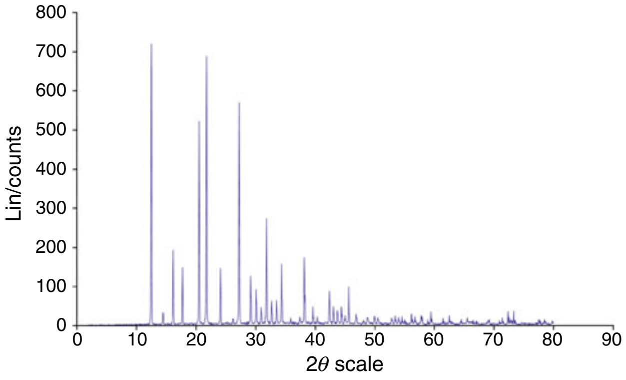

Fig. 1 XRD spectrum of the alum sample

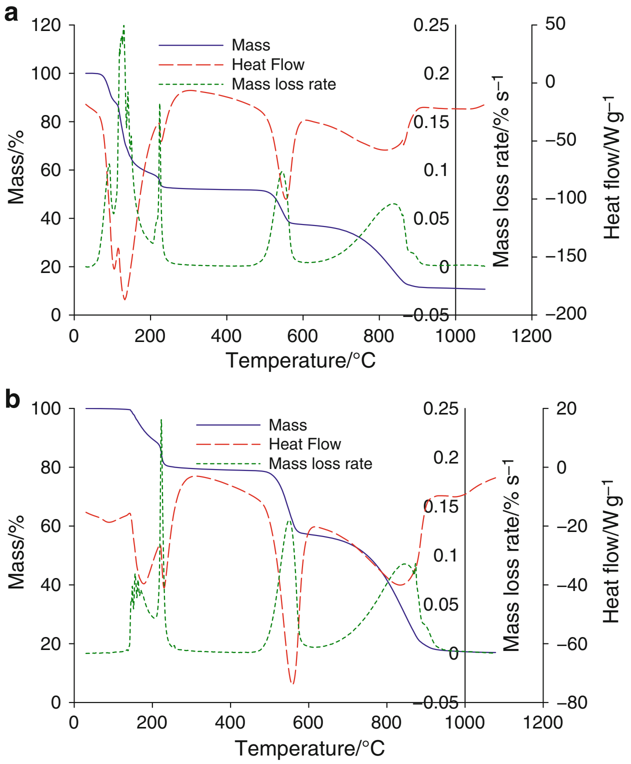

Fig. 2 Overlay of the TG, DSC, and DTG curves obtained from the fresh (**a**) and the annealed (**b**) sample

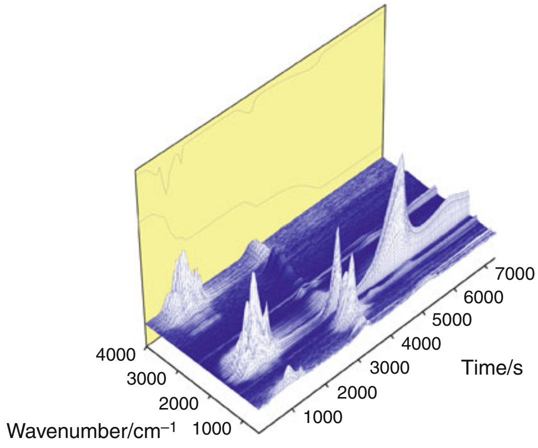

Fig. 3 Overlay of the TG and DTG curves and the FTIR spectra obtained from the gases evolved during the TG experiment with a fresh alum sample

The last degradation step corresponds to the decomposition of the sulfate formed in the 450–600 °C range:

$$(SO_4)_3Al_2 \rightarrow Al_2O_3 + 3SO_2 + 3/2\ O_2,$$

The stoichiometric mass loss related to the sulfate reaction is 26.5% of the initial mass, corresponding to 21.2% to the SO_2, and 5.3% corresponding to the O_2. The theoretical value is practically equal to the drop measured in the last

TG step, 25.1%. Therefore, the proposed reaction can describe correctly the alum degradation.

In order to identify single overlapping processes in the TG results presented above, the generalized logistic mixture model can provide a useful insight [9–12]. The DTG curve was fitted by a mixture of generalized logistic derivatives:

$$y(t)=\sum_{i=1}^{n}\frac{c_i\cdot b_i\cdot\exp(-b_i\cdot(t-m_i))}{[1+\tau_i\cdot\exp(-b_i\cdot(t-m_i))]^{(1+\tau_i)/\tau_i}}$$

where the c parameter represents the mass involved in the degradation process, b is related to the decomposition rate or rate of change, τ accounts for the asymmetry, m represents the temperature at the maximum rate of change, and t is the temperature. The optimal fittings are obtained by minimizing the average squared error (ASE) [9–12].

Figure 4 shows the fitting by a mixture of logistic functions of the DTG curves obtained from the fresh and the preheated samples. The first step is fitted using five logistic components, L1, L2, L3, L4, and L5. This suggests that the water loss and dehydroxylation occurs through five overlapping processes. A deeper study would be necessary to identify each one. The second step is fitted with two logistic components. It indicates that, although a single reaction accounts for this step, the different gases resulting from the reaction may evolve at different rates. The L6 logistic derivative component represents the 4.8% of the initial mass ($c_6 = 4.8$) and may be related to the ammonium and oxygen, while L7 would account for sulfur dioxide and water ($c_7 = 8.9$). In fact, their stoichiometric contents, with respect to the initial mass, are 3.7% of ammonium, 1.7% of oxygen, 7.1% of sulfur dioxide, and 2.0% of water.

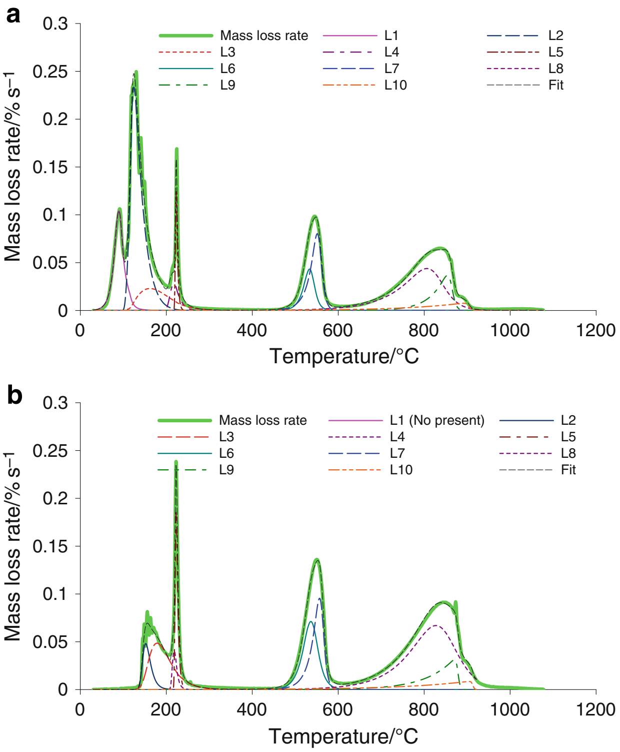

Fig. 4 Plot of the components obtained by fitting of the DTG curves obtained from the fresh (**a**) and the annealed (**b**) sample

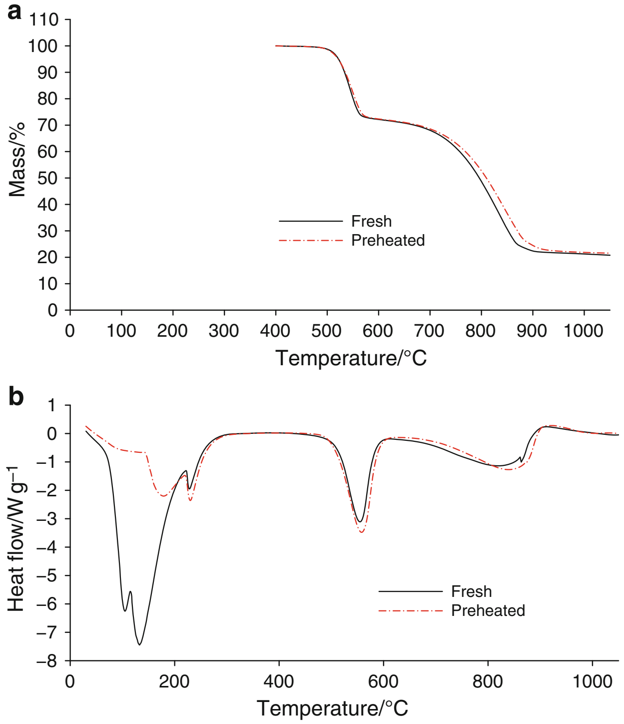

Fig. 5 Overlays of the normalized TG (**a**) and DSC (**b**) curves obtained from the fresh and the annealed sample

Looking at the third degradation step, the percentages of the initial mass obtained by the logistic estimation are 17.63% (estimated by L8), 3.36% (L10), and 5.51% (L9). The L8 and L10 components may represent the amount of sulfur dioxide (21.2%) evolved from the reaction, while L9 would represent the oxygen (5.3%).

Figure 5 shows the overlays of the DSC curves obtained from the fresh and the annealed sample. The TG curves were normalized with respect to the mass at 400 °C. The DSC curves were normalized by baseline subtraction and rotation so that the curves practically match at both the beginning and end of the experiment. The DSC and TG curves for the fresh and the preheated samples are practically equal from 300 °C onward. The only significant differences were observed in the initial degradation step.

Conclusions

Thermal decomposition of hydrated ammonium aluminum sulfate was characterized by simultaneous TG-DSC. Five dehydration processes were identified in the range from 50 to 350 °C leading to anhydrous ammonium aluminum sulfate. Ammonium aluminum sulfate decomposes around 546 °C leading to formation of aluminum sulfate. This process produces ammonia and water, which were identified by FTIR. Finally, aluminum sulfate decomposes around 838 °C producing aluminum oxide and sulfur dioxide. A model based in a mixture of generalized logistic derivative functions supports the chemical reactions described.

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References

1. Alum. In: The Columbia Encyclopaedia, 6th edn. Ithaca, NY: Columbia University Press; 2004. http://www.questia.com/library/encyclopedia/alum.jsp. Accessed 23 Nov 2009
2. D-TER Animal and Bird Repellent. In: Bruce Harris Project Management Pty Ltd. 2004. http://www.bruceharris.com.au/BHPMweb/dter_faq.htm. Retrieved 03 Mar 2010
3. Scat Material Safety Data Sheet. In: Multicrop (Aust.) Pty Ltd. 2003. http://www.multicrop.com.au/MSDS/Scat_MSDS.doc. Accessed 3 Mar 2010.
4. Pest Control: Foxes. In: Tandridge District Council (UK); 2006. http://www.tandridge.gov.uk/environment/pestcontrol/foxes.htm. Accessed 3 Mar 2010.
5. Weast RC. CRC Handbook of Chemistry and Physics, 62nd edn. Boca Raton, FL: CRC Press; 1981. pp. B-74, B-75.
6. Frost RL, Wills RA, Kloprogge JT, Martens W. Thermal decomposition of ammonium jarosite $(NH_4)Fe_3(SO_4)_2(OH)_6$. J Therm Anal Cal. 2006;84:489–96.
7. Frost RL, Wain DL, Wills RA, Musemeci A, Martens W. A thermogravimetric study of the alunites of sodium, potassium and ammonium. Thermchim Acta. 2006;443:56–61.
8. Küçük F, Yildiz K. The decomposition kinetics of mechanically activated alunite ore in air atmosphere by thermogravimetry. Termochim Acta. 2006;448:107–10.
9. Cao R, Naya S, Artiaga R, Garcia A, Varela A. Logistic approach to polymer degradation in dynamic TGA. Polym Degrad Stab. 2004;85:667–74.
10. Naya S, Cao R, López-de-Ullibarri I, Artiaga R, Barbadillo F, García A. Logistic mixture model vs Arrhenius for kinetic study of material degradation by dynamic thermogravimetric analysis. J Chemom. 2006;20:158–63.
11. Barbadillo F, Fuentes A, Naya S, Cao R, Mier JL, Artiaga R. Evaluating the logistic mixture model on real and simulated TGA curves. J Therm Anal Cal. 2007;87:223–7.
12. Pascual J, Corpas FA, López-Beceiro J, Benítez-Guerrero M, Artiaga R. Thermal characterization of a Spanish red mud. J Therm Anal Cal. 2009;96:407–12.