# Study on Montmorillonite Modified by Gluconic Acid as Trace-water Dehydration Materials

Yuanfeng Pan [1,2], Tengyou Wei [2] and Huining Xiao [1] +

[1] Department of Chemical Engineering, University of New Brunswick, Fredericton, NB, E3B 5A3 Canada

[2] Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

**Abstract.** In this work, a new type of trace-water dehydration materials, gluconic acid montmorillonite (GAM), was prepared, in which the alkaline Ca-bentonite was modified by gluconate acid. GAM was characterized by FT-IR, XRD and DSC. The results of structure characterizations indicated that the －OH (hydroxyl groups) content in the GAM was over 16.6wt%. Desorption temperature of water ranged from 50 to 200℃. The layered structure of the alkaline Ca-bentonite was well maintained after the acidic modification with the interlamellar spacing about 1.6nm which is much larger than that of molecular sieves, thus enabling the rapid water absorption at a normal pressure. The results of application in the dehydration of alcohol vapors showed that water concentration in products could be decreased from 5% to 100ppm.

**Keywords:** Trace-water dehydration, montmorillonite, thermal properties, X-ray techniques.

## 1. Introduction

Trace water in organic substances often has a disadvantage over their application in industry. Distillation [1], pervaporation membrane [2] and absorption [3] have been always employed for trace-water dehydration. However, technology of specialty distillation is needed for the system possesses azeotropic point; whereas preparing the membrane with excellent performance to improve the pervasion flux and selectivity is required for pervaporation membrane technology.

Recently, much attention has been paid to the absorption with molecular sieves [4] and biomass absorption [5] as well as a simplified process with improved re-productivity, cleanliness and lower energy consumption. Nevertheless, it is difficult to dehydrate the trace water in the organic substances of small molecule such as methanol, ethanol and acetone using molecular sieves because the selectivity of water adsorption is not particularly high. Meanwhile, the cost of molecular sieves tends to be high and regeneration is difficult. Hassabllah [6] employed corn starch to absorb ethanol vapor with high concentration to obtain anhydrous ethanol. However, the resistance of fluid passing through the sorbent is great and the thermal stability is poor in starch absorption. Therefore, it is important to develop a new kind of gas-phase dehydration materials, which has high absorption capacity and is easy for regeneration, is thermal stable and cost-effective.

The dehydration using alkaline Ca-bentonite has been reported by Qiu et al [7], which reduced the water in ethanol from 5wt% to 0.5wt%. To further enhance the performance of Ca-bentonite, the modification of alkaline Ca-bentonite using gluconic acid was conducted in this work in an attempt to prepare a kind of carbohydrate intercalation bentonite dehydration materials with the improved water absorbing capacity. More importantly, the modified dehydration materials are capable of removing trace water, which can reduce the water content to 100ppm when they were applied for PSA Gas Dehydration of ethanol. Therefore, the

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+ Corresponding author. Tel.: +1-506-453-3532; fax: +1-506-453-3591.
  *E-mail address*: hxiao@unb.ca.

modified alkaline Ca-bentonite could overcome the drawbacks of molecular sieves in dealing with the dehydration associated with small molecules, and has a favorable application prospect.

# 2. Experimental

## 2.1. Materials

Alkaline Ca-bentonite (the moisture content about 8% at 50℃) was self-prepared according to reference [7]. Gluconic acid lactone (GDL) was purchased from Changzhou Zhuoyun Fine Chemical Ltd.. 95% ethanol and absolute ethanol were provided by Huangdong Shantou Xilong Chemical plant and were all analytical-grade.

## 2.2. Characterization techniques

IR spectra were recorded on a Nicolet Magna 550 FTIR spectrophotometer (Tokyo, Japan) set at 4000～400cm-1 with KBr sheeting. XRD was performed using a Rigaku D/MAX2500V diffractometer (Japan) set at 40 kV, 200 mA, $2\theta$ =5°~60° and 5°/min with Cu K$\alpha$ radiation ($\lambda$=1.54056 Å). DSC measurements were conducted with a PerkinElmer (DSC6200) thermal analyzer (USA). The samples were heated up to 600°C at a rate of 10°C/min. Water content was determined by DL38 Card's Moisture Meter (Switzerland).

## 2.3. Preparation of trace-water dehydration materials

10.0g alkaline soil and a chosen amount of ethanol at a certain concentration were placed into a three-neck flask equipped with a mechanical stirrer, dropping funnel and condenser. An appropriate amount of 30% GDL solution was added dropwise under a certain temperature and constant stirring for 1h to react with alkaline soil. After the completion of GDL feeding, the mixture was kept reacting for 1~5h, then filtrated, washed repeatedly with ethanol aqueous solution and dried under vacuum at 50℃.

## 2.4. Trace-water dehydration of ethanol vapor

21.2 g GAM with mean particle diameter of 2~4 mm were packed into the absorption column, whose diameter, height and effective load height were 10mm, 550mm and 450mm, respectively; and then placed into a thermostated jacket. The GAM were activated and regenerated at 0.005 MPa and 90 ℃ for 3h before the dehydration experiment, in which the ethanol containing 5% water were heated to vaporize at a certain voltage. The vapor passed through the GAM in the column and was collected when it exited into the condenser. The water content of the condensate products was then measured.

# 3. Results and discussion

## 3.1. Characterization of GAM as dehydration materials

Figure 1 exhibits the FT-IR spectra of GAM and alkaline soil. The typical absorption peak of $Ca^{2+}$ and the stretch vibration peak of -OH of GAM occur at 1451.6 $cm^{-1}$ and 3412.9 $cm^{-1}$ respectively, which shows that GAM possess some properties of original alkaline soil and absorb –OH by inner surface as alkaline soil. The $OH^-$ typical absorption peak of alkaline soil at 2515 $cm^{-1}$ is essentially absent, and that at 1794 $cm^{-1}$ and 876 $cm^{-1}$ weakens in the GAM. Whereas, the weak absorption peak of 1269.2 $cm^{-1}$ represents the stretch vibration peak of C-O. The results above demonstrated that gluconic acid group had already reacted with alkaline soil and GAM possessing more –OH had been obtained. It is also shown by the measurement of ignition loss that the gluconic acid content is over 20 wt% and the corresponding hydroxyl content is up to 16.6% in the GAM.
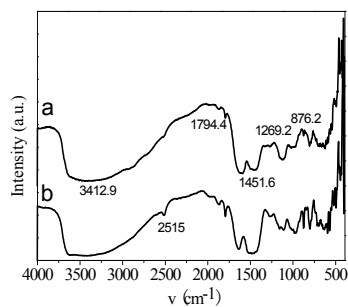
Fig. 1: IR spectra of dehydration materials: (a) GAM; (b) alkaline Ca-bentonite.

XRD results for 5A molecular sieves, alkaline soil and GAM are illustrated in Figure 2. The interlamellar spacing of the GAM and alkaline Ca-bentonite, calculated from the peak of D001 in Figure 2, are all 1.6nm, which showed that the increasing of –OH groups in the layers of montmorillonite did not change their layered structure. Whereas, the interlamellar spacing of the 5A molecular sieves is below 0.5nm. The results indicated that the interlamellar spacing of the GAM and alkaline Ca-bentonite is much larger than that of 5A molecular sieves, thus allowing them to absorb and dehydrate water rapidly. In addition, the dehydration selectivity was improved when alkaline Ca-bentonite as well as modified alkaline Ca-bentonite was used in gas absorption at a normal pressure.
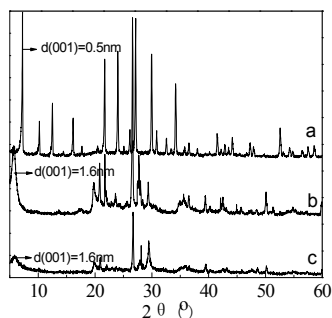


Fig. 2: X-ray diffraction patterns of dehydration materials: (a) 5A molecular sieves; (b) alkaline Ca-bentonite; (c) GAM.

Figure 3 displays the DSC curves of 5A molecular sieves, alkaline soil and GAM, respectively. The curves show that their frameworks are all stable in the range of the temperature measured. The temperature of dehydration-absorption peak for GAM and alkaline soil are both at 110℃, while for 5A molecular sieves at 250℃. The higher the temperature of the dehydration endothermic peak, the more difficult the regeneration of dehydration materials. Therefore, the regeneration of 5A molecular sieves is far more difficult than that of GAM and alkaline soil.
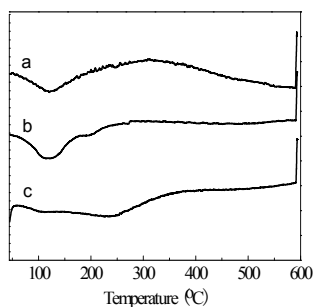


Fig. 3: DSC curves of dehydration materials: (a) GAM; (b) alkaline Ca-bentonite; (c) 5A molecular sieves.

## 3.2. Trace-water dehydration of alcohol vapor

The absorption penetrating curves of alcohol vapor are shown in Figure 4. The absorption process was operated at 95v using the GAM regenerated once and ten times. Finally, 15g of alcohol containing 100ppm water was obtained after the dehydration with 21.2g of the products. The dehydration capacity of GAM is still excellent after the materials are regenerated at 0.005 MPa and 90℃ for 3h ten times.
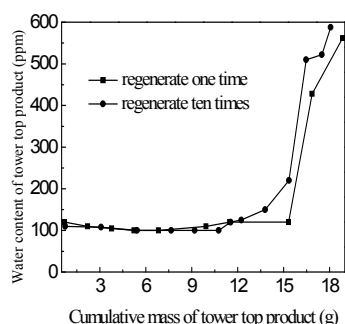


Fig. 4: Water content change of tower top alcohol as cumulative mass of tower top product.

## 4. Conclusions

The modified trace-water dehydration materials, GAM, were prepared. Compared with 5A molecular sieves, the interlamellar spacing of the prepared dehydration materials is about 1.6 nm which is much larger than the aperture of sieves. The modified dehydration materials have several advantages over the conventional molecular sieves, including the faster diffusion rate, higher water absorption, more stable structure, easier regeneration, and lower pressure required for vapor absorption with transformation. Furthermore, alcohol containing water as low as 100ppm could be obtained after their vapor passed through the GAM, in which the absorption velocity is fast, the energy expenditure is low, the regeneration is easy and the pollution is eliminated. Therefore, the modified dehydration is very promising with the great in the field of trace-water removal.

## 5. Acknowledgements

## 6. References

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