J Therm Anal Calorim (2012) 109:945–950
DOI 10.1007/s10973-011-1825-x

Thermal analyses of home-made zeolite by DSC and TG

**Sheng-Hung Wu · Chu-Chin Hsieh ·
Chung-Cheng Chiang · Jao-Jia Horng ·
Wei-Ping Pan · Chi-Min Shu**

Received: 30 June 2011 / Accepted: 27 July 2011

Abstract Volatile organic compounds (VOCs) and greenhouse gases are the main factors involved in pollution control and global warming. Various treatment methods involving incineration, adsorption, etc., have been employed to reduce VOCs and greenhouse gases concentration in the operating environment and atmosphere. Activated carbon, zeolite, silica gel, and alumina have been broadly used to adsorb pollutants in various industrial applications. Based on the promising effect of adsorption, we analyzed and identified the thermal phenomena of home-made zeolite using various instruments. The endothermic reaction under 100 °C of home-made zeolite was identified as steam adsorption, which is an important discovery. The optimal adsorption temperatures of home-made zeolite have been determined at 200–550 °C.

Keywords Activated carbon · Greenhouse gases · Home-made zeolite · Steam · Thermal phenomena · Volatile organic compounds (VOCs)

Introduction

Carbon dioxide (CO_2) (65% in green house gases) and volatile organic compounds (VOCs) are commonly target pollutants worldwide that have caused global warming and environmental pollution. VOCs have adverse effects on human health, cause odorous nuisances, and participate in photochemical reactions. The purification of industrial waste gases containing VOCs plays an important role in chemical engineering [1–4]. Activated carbon, zeolite, silica gel, and alumina have been broadly employed to adsorb VOCs in the petrochemical, semiconductor industries, and household applications.

Zeolite has been widely used in various industrial fields, and it has generally been used in the form of beads or pellets. Many studies have applied various types of zeolite to analyze the adsorption effect for VOCs chemicals and the adsorption capability with various formats of zeolite [5–9]. In essence, industries have handled zeolite to adsorb VOCs or pollutants in the zeolite rotor-wheel system. The zeolite rotor-wheel system is full of zeolite and was planned as two areas involving adsorption and desorption zone. When the adsorption zone is full of VOCs, the rotor-wheel system is turned to another side that will proceed desorbing procedure. At the same time, the adsorption zone continues to adsorb the pollutants. Therefore, the desorption zone is a dangerous area regarding VOCs mixed with high oxygen concentration that have caused many serious runaway reactions or fire accidents. Industries are widely using nitrogen (N_2) as purge gas, when high O_2 concentration

---

S.-H. Wu (✉)
Department of Fire Science, WuFeng University, 117, Chian-Kuo Rd., Sec. 2, Min-Hsiung, Chiayi 62153, Taiwan, ROC
e-mail: wushprofessor@gmail.com

C.-C. Hsieh · J.-J. Horng · C.-M. Shu
Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology (NYUST), 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan, ROC

C.-C. Chiang
Department of Electrical Engineering, Hsiuping Institute of Technology (HIT), 11, Gongye Rd., Dali Dist, Taichung 41280, Taiwan, ROC

W.-P. Pan
Institute for Combustion Science & Environmental Technology, Western Kentucky University, Bowling Green, KY 42101, USA

exists in the desorption zone. This study was used to analyze the thermal behavior of home-made zeolite by thermogravimetric analyzer (TG) in air (21 vol.% O_2) and nitrogen (N_2) (0 vol.% O_2).

Zeolite is a quite stable adsorbent and was analyzed including an endothermic reaction below 100 °C [10]. This study was applied to analyze the endothermic reaction and thermal behavior using differential scanning calorimetry (DSC), TG, mass spectrometer (MS), Brunauer–Emmett–Teller (BET), and X-ray Diffraction (XRD). Results indicated that the endothermic reaction is adsorbing steam.

Experimental design and methods

Samples

Home-made zeolite was applied as five steps, including mixing, gelling, forming, drying, and calcining. Manufacturing procedure was described as follows:

(a) Mixing: SiO_2 and sodium silicoaluminate powder were mixed as various Si/Al ratios.
(b) Gelling: Sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were widely applied as gelling solution. Among them, NaOH was selected for use in this study.
(c) Forming: Zeolite was put into the extruding forming machine. Sphere, tablet, pellet, extrudate, granule, flake, and bead are common forms of adsorbent.
(d) Drying: Zeolite was dried under 100 °C for 8 h in oven.
(e) Calcining: This study is the final process that was applied to calcine zeolite under 450 °C for 10 h in oven.

This study was used to manufacture various Si/Al ratios involving 20–90% that were enforced to analyze the best Si/Al ratio using calorimeter.

DSC

Method 1

The sample was analyzed by a TA Q-2000 DSC. The sample was equilibrated at 30 °C, then heated to 550 °C at the rate of 4 °C min^{-1}, and then cooled to 30 °C at the rate of 10 °C min^{-1}, and heated to 550 °C at the rate of 4 °C min^{-1} again. The sample was analyzed with a pinhole pan. The experiment took place in the air atmosphere with the heat flow of 50 mL min^{-1}.

Method 2

The sample was equilibrated at 200 °C, isothermal for 60 min, then cooled to 30 °C at a rate of 10 °C min^{-1}, and then heated to 550 °C min^{-1} at a rate of 4 °C min^{-1}, and cooled to 30 °C at a rate of 10 °C min^{-1}, and heated to 550 °C at a rate of 4 °C min^{-1}. The sample was analyzed with a pinhole pan. The experiment took place in the air atmosphere with the heat flow of 40 mL min^{-1}.

Method 3

Scanning experiments were carried out on a Mettler TA8000 System coupled with a DSC821^e measuring cell. STAR^e software was applied for acquiring curve traces. An aluminum standard pan was employed to avoid evaporation of the home-made zeolites during the scanning experiment. For better accuracy in testing, the scanning rates chosen for the temperature range were from 30 to 550 °C with 4 °C min^{-1} under atmospheric air. Reactions can be investigated within 30–550 °C, for the working temperature range of this thermostat. DSC is regarded as a useful tool for the evaluation of thermal hazards and for the investigation of decomposition mechanisms of reactive chemicals if the experiments are carried out carefully. The experimental conditions were set as follows:

(a) Heating rates: 4 °C min^{-1}.
(b) Materials mass: 1–20 mg.
(c) Test cell: An aluminum standard pan was used to avoid evaporation for the various Si/Al ratios of home-made zeolites during scanning experiment [11–15].

TG

The sample was analyzed by a TA Q-5000 TGA. The sample was equilibrated at 30 °C, isothermal for 20 min, and then heated to 900 °C at a rate of 4 °C min^{-1}. The experiment was conducted under N_2 and air flow with total flow maintained flow of 35 mL min^{-1}.

Thermogravimetric analysis–mass spectrometry (TG–MS) technique

The sample was analyzed by a TA 2950 TG interfaced to a Pfeiffer Thermostar mass spectrometer (MS) by means of a heated capillary transfer line. In this system, the sample was equilibrated at 30 °C and then heated to 640 °C at a rate of 4 °C min^{-1} under air flow. The capillary transfer line was heated to 200 °C, and the inlet port on the MS was heated to 150 °C. The Thermostar unit is based on a quadrupole design, and the mass scan ranges from 0 to 300 amu. The sample gas from the TG was ionized at 70 eV. The system was operated at a pressure of 1×10^{-5} torr. The experiment was performed in air with flow rate of 100 mL min^{-1}.

XRD technique

The samples were analyzed using ARL Thermo X-ray diffraction meter measurements. The sample was swept from $2\theta = 3°$ to 50° with a speed of 0.5° min^{-1}. The X-ray generator was set to 20 kV and 20 mA. The sample was scanned at 40 and 200 °C, and the residue was also scanned at the same condition. The experiment took place under air atmosphere with the flow rate of 300 mL min^{-1}.

BET technique

The samples were degassed at 150 °C for 5 h in a vacuum. Then they were run on a Micromeritics ASAP 2020 surface area analyzer. The surface area was calculated using multipoint BET equation in the relative pressure range of 0.05–0.3.

Results and discussion

DSC investigations

For DSC experiment, there are two methods. For the method 1, in the first heat run, there is an endothermic peak around 100 °C, which was due to the evaporation of water (which is proven by TG–MS); then at 380 °C, there was a spike because there was so much moisture evolved, which built the pressure in the sample pan and caused the leaking in the pan. Therefore, a good way to solve the problem is to remove the moisture first and then run the sample again. Therefore, the sample was analyzed by method 2.

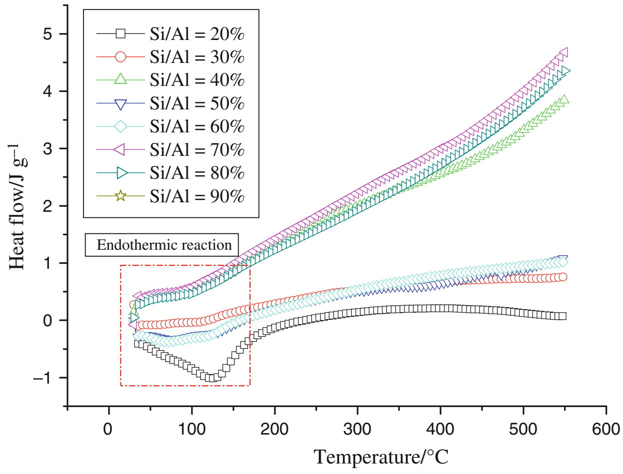


Fig. 1 Thermal behavior for various Si/Al ratios of home-made zeolites by DSC under 4 °C min^{-1} heating rate

Table 1 Heat of endothermic reaction, mass loss parameters, and BET test of home-made zeolite

Si/Al ratio	ΔH_{endo} by DSC in air/J g^{-1}	Mass loss by TG in N_2/%	Mass loss by TG in air/%	BET/ $\text{m}^2\ \text{g}^{-1}$
20	162	16	16	462
30	32	6	10	204
40	89	8	9	159
50	100	3	9	140
60	117	7	9	114
70	115	7	8	100
80	130	8	5	94
90	82	6	8	94

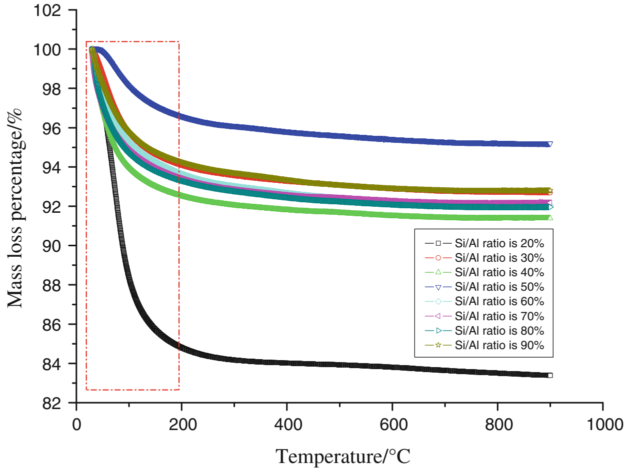


Fig. 2 Thermal analyses of various Si/Al ratios by TG (in N_2)

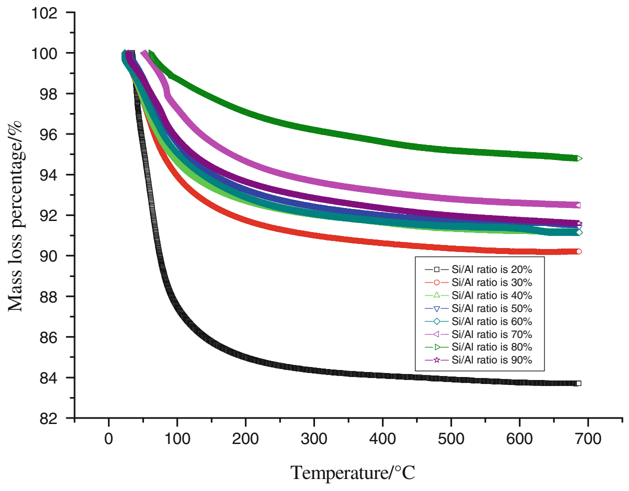


Fig. 3 Thermal analyses of various Si/Al ratios by TG (in air)

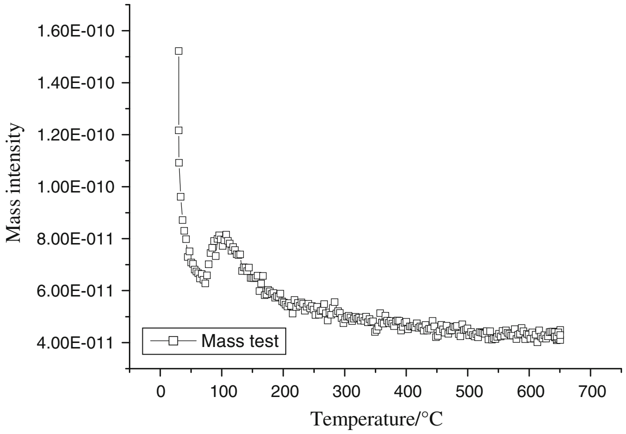


Fig. 4 The $m/z = 18$ MS plot of the zeolite sample under air flow by TG–MS

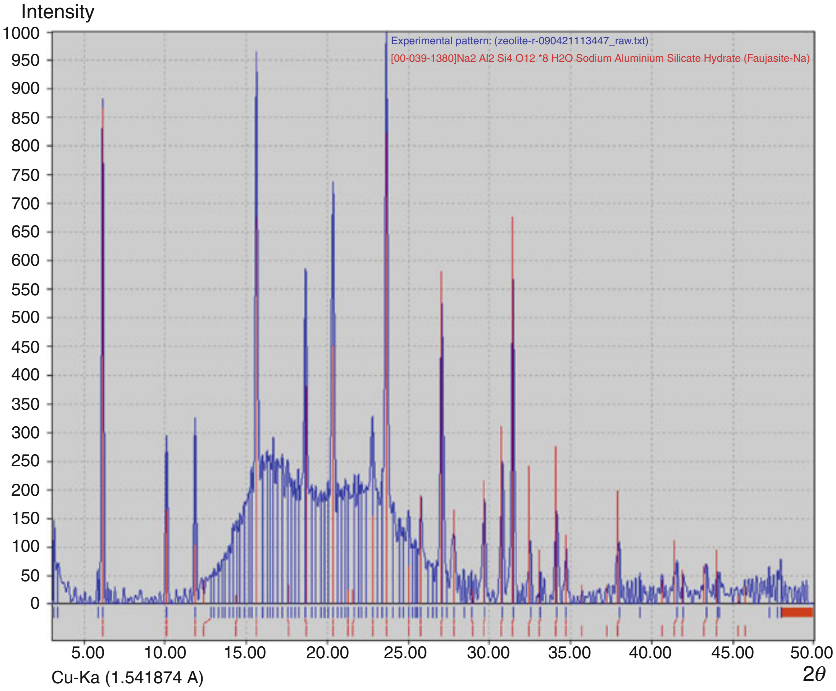
The sample was directly heated to 200 °C to remove the water, isothermal for 60 min, and then heated to 550 °C at the rate of 4 °C min^{-1}, in which the first heat run referring to that sample was heated from 30 to 550 °C after isothermal at 200 °C for 60 min, and for the second heat run referring to that after the first heat, the sample was cooled to 30 °C and heated to 550 °C at the rate of 4 °C min^{-1} again. The DSC results showed that maybe there is a transition at the first heat run, but it is difficult to make sure what the transition is. At the second run, there was a glass transition at 200 °C since the sample had become amorphous.

Figure 1 displays thermal behaviors of various Si/Al ratios home-made zeolite by DSC in air gas. DSC was applied to evaluate thermal decomposition behaviors of home-made zeolite. Zeolite is the best adsorbent in VOCs or pollution, but its thermal characteristic is more important. According to thermal curves, home-made zeolite has an endothermic reaction before 100 °C. The endothermic reaction was analyzed that is adsorbing steam of air. Home-made zeolite under 100–550 °C of DSC tests in this study was the best adsorption range, because it is not decomposed. Process engineers must notice oxygen concentration in adsorption area. Oxygen concentration of this area must be controlled under lower flammability limit (LFL) or lower explosion limit (LEL) of VOCs. Main reason of combustion accident was analyzed regarding oxygen concentration in adsorption area.

Heat of endothermic reaction (ΔH_{endo}) by DSC and mass loss percentage by TG in N_2 and air of various Si/Al rations home-made zeolite were determined and listed in Table 1. 20% of Si/Al of home-made zeolite was investigated as inferior ratio that had 16% mass loss by TG in N_2 and air. The BET test of 20% Si/Al was to be 462 $\text{m}^2\ \text{g}^{-1}$. 20% of Si/Al of home-made zeolite was analyzed that has a large surface to adsorb the steam. The results indicated that home-made zeolite was used to heat over 100 °C before adsorbing the VOCs.

In general, activated carbon is a traditional adsorbent that is widely used to adsorb the waste in water or air, but it has a flame problem in chemical industries. The price of activated carbon is cheaper than the zeolite. Exothermic onset temperature (T_o) of activated carbon was discovered to be 400 °C by DSC. The endothermic behavior of activity carbon was determined by DSC under 100 °C. Activated

Fig. 5 Structure analysis for 20% Si/Al home-made zeolite by XRD spectrum



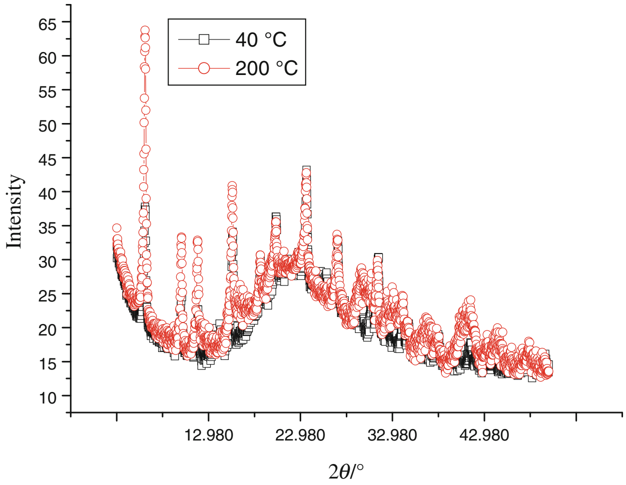


Fig. 6 XRD spectrum of the home-made zeolite sample at 40 and 200 °C

carbon has a violent profile exceeding 400 °C that was evaluated to be thermal hazard in chemical application. Therefore, heat of decomposition (ΔH_d) of activated carbon was integrated about 19,200 J g^{-1} by DSC [10].

TG analyses

This study was used to analyze various Si/Al ratios by TG in N_2 and air. According to Fig. 2, 20% of Si/Al was investigated that had 16% mass loss. 30, 40, 60, 70, 80, and 90% of Si/Al were discovered that have 6–8% mass loss. Results indicated that the best ratio of Si/Al was 50 considering only 3% mass loss. The mass loss curve and mass loss rate curve for the zeolite sample under air flow are plotted in Fig. 3. Thermal behavior of home-made zeolite by TG in N_2 or air was discovered as similar.

The mass peak for each evolved gas was correlated with the derivative thermogravimetric (DTG) curve. The evolution of each gas can be matched with the DTG curve for the analysis of time and temperature of evolution and the mass percentage. The mass no. 18 may be due to the evolution of water (Fig. 4). Water evolution started at the beginning and reached a peak maximum temperature at 60 and 69 °C in air and nitrogen, respectively, which may come from the moisture presented in the sample. Here, water continued to be released.

XRD explanations

The sample was ground into powder for the XRD test. The XRD spectrum of the 20% Si/Al home-made zeolite sample matched the standard spectra of Faujasite-Na ($Na_2Al_2Si_4O_{12}\cdot 8H_2O$), as illustrated in Fig. 5. Compared with the original XRD spectra at 40 °C, the intensity/crystallization of the main peaks increased (Fig. 6) likely due to loss of water as evidenced in the TG data. When the temperature increased to 300, 400, 500, 550, and 640 °C, the intensity of the main spectrum peaks decreased and the peaks became wider, which is attributed to a more amorphous structure than the starting material as the temperature was increased. Although the XRD results showed that the main composition is Faujasite-Na at room temperature, heating the sample results in loss of crystallinity and an increase in amorphous content as evidenced by the shifting and broadening of the peaks.

Conclusions

Home-made zeolite is a quite stable adsorbent and has fulfilled the aim of lowering cost for various industries. Home-made zeolite has an endothermic reaction that has been proven as steam adsorption. Zeolite must be desorbed at exceeding 100 °C, when it will be handled to adsorb VOCs in the zeolite rotor-wheel system. Therefore, results indicated that the endothermic reaction of home-made zeolite is adsorbing steam according to MS test. The BET test of 20% Si/Al was calculated to be 462 m^2 g^{-1} which is a large surface to adsorb the VOCs. The XRD spectrum of the zeolite sample matched the standard spectra of Faujasite-Na ($Na_2Al_2Si_4O_{12}\cdot 8H_2O$).

Acknowledgements The authors are indebted to the donors of the Ministry of Economic Affairs in Taiwan under the contract No. EC-17-A-10-S1-113 for financial support.

References

1. Chen CL, Fang HY, Shu CM. Source location and characterization of volatile organic compound emissions at a petrochemical plant in Kaohsiung, Taiwan. J Air Waste Manag Assoc. 2005;55:1487–97.
2. Chen CL, Shu CM, Fang HY. Location and characterization of VOC emission at a petrochemical plant in Taiwan. Environ Forensics. 2006;7:1–9.
3. Chen CL, Fang HY, Shu CM. Mapping and profile of emission sources for airborne volatile organic compounds from process regions at a petrochemical plant in Kaohsiung, Taiwan. J Air Waste Manage Assoc. 2006;56:824–33.
4. Salden A, Eigenberger G. Multifunctional adsorber/reactor concept for waste-air purification. Chem Eng Sci. 2001;56:1605–11.
5. Breck DW. Zeolite molecular sieves—structure chemistry and use. New York: Wiley; 1974.
6. Dyer A. An introduction to zeolite molecular sieves. New York: Wiley; 1988.
7. Yuranov I, Renken A, Kiwi-Minsker L. Zeolite/sintered metal fibers composites as effective structured catalysts. Appl Catal A. 2005;281:55–60.
8. Meininghaus CKW, Prins R. Sorption of volatile organic compounds on hydrophobic zeolites. Microporous Mesoporous Mater. 2000;35–36:349–65.

9. Ichiura H, Nozaki M, Kitaoka T, Tanaka H. Influence of uniformity of zeolite sheets prepared using a papermaking technique on VOC adsorptivity. Adv Environ Res. 2003;7:975–9.
10. Su CH, Wu SH, Shen SJ, Shiue GY, Wang YW, Shu CM. Thermal characteristics and regeneration analyses of adsorbents by differential scanning calorimetry and scanning electron microscope. J Therm Anal Calorim. 2009;96:765–89.
11. Wu SH, Chi JH, Huang CC, Lin NK, Peng JJ, Shu CM. Thermal hazard analyses and incompatible reaction evaluation of hydrogen peroxide by DSC. J Therm Anal Calorim. 2010;102:563–8.
12. Shen SJ, Wu SH, Chi JH, Wang YW, Shu CM. Thermal explosion simulation and incompatible reaction of dicumyl peroxide by calorimetric technique. J Therm Anal Calorim. 2010;102:569–77.
13. Lin WH, Wu SH, Shiu GY, Shieh SS, Shu CM. Self-accelerating decomposition temperature (SADT) calculation of methyl ethyl ketone peroxide using an adiabatic calorimeter and model. J Therm Anal Calorim. 2009;95(2):645–51.
14. Huang CC, Peng JJ, Wu SH, Hou HY, You ML, Shu CM. Effect of cumene hydroperoxide on phenol and acetone manufacturing by DSC and VSP2. J Therm Anal Calorim. 2010;102:579–85.
15. Wu SH, Wang YW, Wu TC, Hu WN, Shu CM. Evaluation of thermal hazards for dicumyl peroxide by DSC and VSP2. J Therm Anal Calorim. 2008;93:189–94.