Polyimide grafted magnesium hydroxide for CO_2 Adsorption

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폴리이미드 그라프팅 수산화마그네슘의 이산화탄소 흡수

푸시파라지 헤마라다, 마니 가네쉬, 팽메이메이, 김대경, 장현태
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Abstract

Polyimide (PI) grafted magnesium hydroxide was synthesised and characterised by XRD, TGA, SEM analysis. XRD patterns of PI/$Mg(OH)_2$ carried the peaks due to $Mg(OH)_2$ with decreased intensity. The CO_2 adsorption capacity of PI/$Mg(OH)_2$ at 50°C was found to be 14 wt% revealing chemisorption of CO_2 on $Mg(OH)_2$ which could be regenerated at higher temperatures.

Keywords: Magnesium hydroxide, polyimide, composite, CO_2 adsorption,

1. Introduction

Carbon dioxide capture and geologic storage offer a new set of options for reducing greenhouse gas emissions that can complement the current strategies of improving energy efficiency and increasing the use of non-fossil energy resources. The membrane technology for both pre- and post-combustion separation of CO_2 and adsorption/absorption technologies are the explored capture methods. CO_2 adsorption on oxides and mixed oxides[1-3], high surface area porous materials including zeolites[4,5] carbon[6], metal-organic frameworks(MOFs)[7], amine dendrimers and amine functionalized mesoporous silicas[8] are currently being studied. Inaddition, porous polymer were also employed, in particular polyimide (PI) membranes obtained by the reaction between an aromatic dianhydride and aromatic diamine are used in the separation processes. Recently Sixin and Xinhai [9] studied the PI grafted magnesium hydroxide as a flame retardant material. As the metal oxide and PI separately exhibited a good CO_2 capturing property, in this present study a porous PI together with an alkaline metal hydroxide i.e.$Mg(OH)_2$ was synthesised and tested for CO_2 adsorption.

2. Experimental

Materials and method

3,3',4,4'-biphenyl tetracarboxylic dianydride, BPDA (Aldrich), *p*-phenylenediamine, PDA (Daejung), magnesium hydroxide, $Mg(OH)_2$ (Junsei chemical), trimethoxysilane, TMOS(Aldrich), *p*-toluenesulfonic acid (Daejung) were used.The solvents used are dimethylacetamide, DMAc (Samchun) and toluene (Samchun). The PI intercalated $Mg(OH)_2$ was prepared by adopting the procedure of Sixin and Xinhai[9].Typically, a reaction mixture containing PDA, TMOS and DMAc in a mole ratio of 1:1:15 were stirred for 24h at room temperature. $Mg(OH)_2$ was then added to the above mixture and stirring was continued for 30min followed by the addition of BPDA (1mole). The mixture was

further stirred for 2 h at room temperature. 0.05 wt% of *p*-toluene sulfonic acid and toluene (15ml) was added. The reaction mixture was refluxed for 6-8 h, cooled to room temperature, filtered and dried. The material is designated as PI/$Mg(OH)_2$.

Catalyst characterization

Powder X-ray diffraction pattern (XRD) were recorded on Rigaku Miniflex diffractometer using a Cu-Kα radiation (λ=0.154 nm). The diffraction data were recorded in the 2Θ range 5 to 50° with a step size of 0.02 and a steptime of 1s.The thermogravimetric analysis (TGA) was carried out in a N_2 atmosphere at a flowrate of 40 ml/m in on a SCINCON-1000 thermogravimetric analyzer, by heating *ca.* 10 mg of the sample from 25 to 700 °C in steps of 10 °C/min. The morphologies of the samples were studied using a JEOL JSM5600 scanning electron microscope (SEM) with an energy dispersive X-ray analysis (EDS) detector.

CO_2adsorption

CO_2adsorption - desorption measurements using high purity CO_2 (99.999%) and N_2 for synthesised material were performed using TGA. A sample weight of *ca.* 10 mg was loaded into an alumina sample pan in a TG unit and the initial activation was carried out at 300 °C for 1 h under a N_2 atmosphere. Then the temperature of sample was brought down to 50 °C for CO_2 adsorption. Desorption was conducted by gradually raising the temperature from 50 °C to 300 °C by passing N_2. CO_2 and N_2 were passed through an automatic valve, assisted with a timer for continuous adsorption or desorption profile.

3. Results

3.1 Test Results

Figure 1 shows the wide angle X-ray diffraction of PI, $Mg(OH)_2$, PI/$Mg(OH)_2$. The intensity of the peaks due to $Mg(OH)_2$ is decreased and the peaks due to pristine polyimide is not evident in the PI/$Mg(OH)_2$.This shows that the grafted polyimide is well dispersed inbetween the $Mg(OH)_2$ layers. The thermograms of PI, $Mg(OH)_2$ and PI/$Mg(OH)_2$ are presented in Fig.2. The weight loss observed for $Mg(OH)_2$ and PI/$Mg(OH)_2$ in the temperature range of 350-430 °C is attributed to the decomposition of $Mg(OH)_2$.The overall weight loss was determined to be around 27.5 and 28.8% for $Mg(OH)_2$ and PI/$Mg(OH)_2$ respectively (at 430°C), which is slightly less than the reported weight loss of 31.04% for the complete decomposition of $Mg(OH)_2$ [10]. The reported weight loss in the present work is in agreement with the previous reports on $Mg(OH)_2$ to MgO transformation [11,12]. The weight loss in the high temperature range above 600 °C is attributed to decomposition of polyimide. The SEM image of the synthesised material is presented in Fig.3 illustrated spongy like morphology.

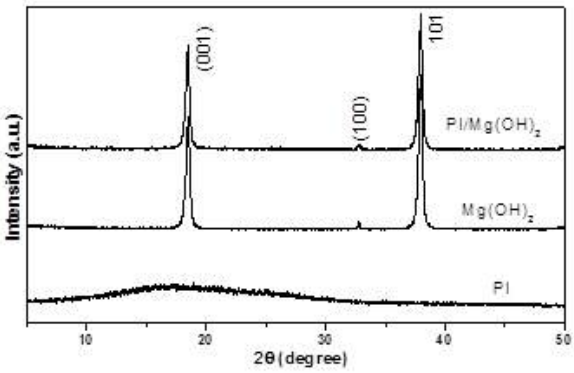

Fig.1. X-ray diffraction patterns of the synthesised materials

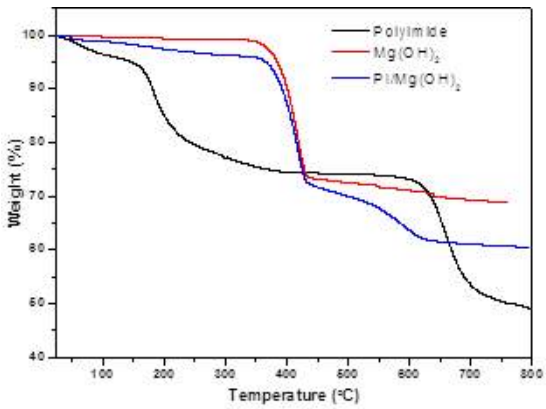

Fig.2. Thermograms of the synthesised materials

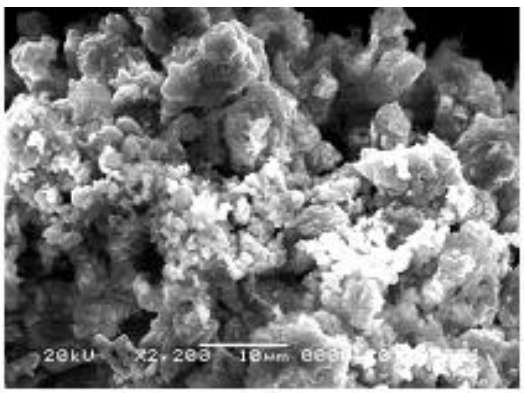

Fig.3. SEM image of PI/$Mg(OH)_2$

CO_2 adsorption: CO_2 adsorption/desorption profile of PI/$Mg(OH)_2$ at 50 °C is depicted in Fig. 4. The maximum CO_2 adsorption capacity was found to be 14 wt%. This increase in weight uptake is attributed to both physisorption and chemisorption of CO_2 with $Mg(OH)_2$. Complete desorption of CO_2 was not observed at the set regeneration temperature of 300 °C evidencing chemisorption of CO_2.

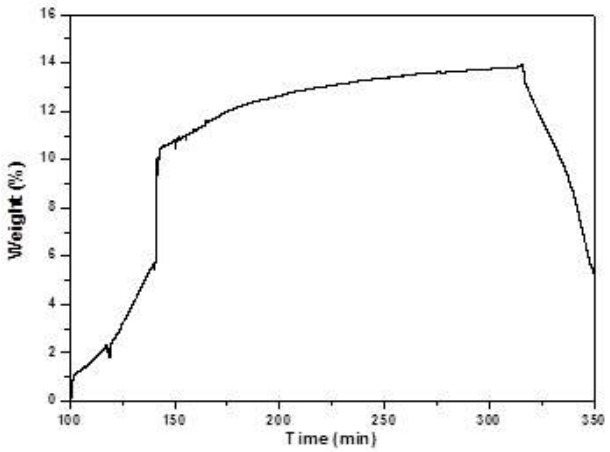

Fig.4. CO_2 adsorption-desorption profile of PI/$Mg(OH)_2$

4. Conclusions

Polyimide grafted magnesium hydroxide was successfully synthesised and tested for CO_2 adsorption. The synthesised material possessed the characteristic peaks in the XRD pertaining to $Mg(OH)_2$. The CO_2 adsorption studies on the composite material shows the maximum CO_2 uptake of 14 wt% which is more than that of pure $Mg(OH)_2$ as well as polyimide. From this study, it is concluded that the prepared PI/$Mg(OH)_2$ is better choice of sorbent to capture CO_2 from the flue gas at low temperature.

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