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Performance of layered birnessite-type manganese oxide in the thermal-catalytic degradation of polyamide 6

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ABSTRACT

The nature and the extent of degradation of polyamide 6 (PA6) in the presence of layered birnessite-type manganese oxide (LMO) were analysed by thermogravimetric analysis under static air atmosphere at several heating rates between 5 °C/min and 20 °C/min. The samples were characterized using infrared (IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 gas adsorption–desorption and thermal analysis (TA) techniques. XRD and DTA results for LMO showed that the oxidative transformation of MnO_2 was occured on heating from 300 °C to 500 °C. The IR spectra of Mn–O band proved the covalent character of oxygen bonding to the metal ions of the surface. The addition of LMO caused the change in the crystalline phase of PA6 from predominantly α to largely γ phase. The activation energy for degradation estimated by Kissinger method for PA6 and 10 wt.% LMO/PA6 composite were found to be 213 and 118 kJ/mol in static air atmosphere, respectively. The experimental results revealed that the addition of 10 wt.% LMO decreased the thermal stability in static air of PA6 by about 80 °C.

1. Introduction

Thermal degradation of polymers have drawn attention because of their importance in the conversion of waste polymers to useful chemical or fuels [1–3]. Pure thermal degradation of waste polymers requires high temperatures and results in a wide variety of products. The addition of a catalyst improves the quality of products obtained from decomposition of polymers and reduces the temperature of decomposition [4,5].

Polyamides (PA) are an important group of the thermoplastic polycondensates. The amide group can be obtained by polymerization of lactams or by condensation of diamines with dicarboxilic acids. The thermal degradation of polyamides were studied systematically in the past [6,7]. The mechanistic studies about the thermal degradation products of polyamides showed that the thermal degradation was initiated by hydrogen abstraction from the methyl-group adjacent to the nitrogen atom and propagated by oxidation of the formed macroradical [6,7]. Karstens and Rossbach [6,7] proposed a detailed degradation scheme starting with oxygen attack at the N-vicinal methylene group (Scheme 1). The mechanism was supported by many other authors [8–12].

Manganese oxides are reported to be among the most efficient oxide solids for catalytic oxidation reactions such as the selective catalytic reduction of NO*x* with NH_3 [13], the catalytic decomposition of ozone [14], the catalytic combustion of volatile organic compounds [15] and catalytic decoposition of polymers [16–18]. This behavior is attributed to the variable electronic structure and oxidation state in a variety of compounds (MnO_2, Mn_2O_3 and Mn_3O_4), which shows good redox properties.

Solid acid catalysts, such as manganese oxides, promote hydrogen transfer reactions due to the presence of many acid sites. A careful analysis of the existing literature indicates that not many studies have been conducted at understanding the catalytic thermal degradation pathway of PA6 using manganese oxides. The role of manganese oxide catalysts in oxidation reactions prompted us to study the effect of this catalysts on PA6 degradation reactions. Taking into account this background, layered birnessite-type manganese oxide (LMO) was synthesized and evaluated in the catalytic thermal degradation of PA6. Infrared (IR) decomposition studies of PA6 on LMO were performed to get a better insight in the degradation mechanism.

2. Experimental

2.1. Materials and sample preparation

PA6 pellets used in this study were obtained commercially from Resinex. Other chemicals were of >99.9% purity or of analytical grade, and purchased from Sigma–Aldrich Co. and used without

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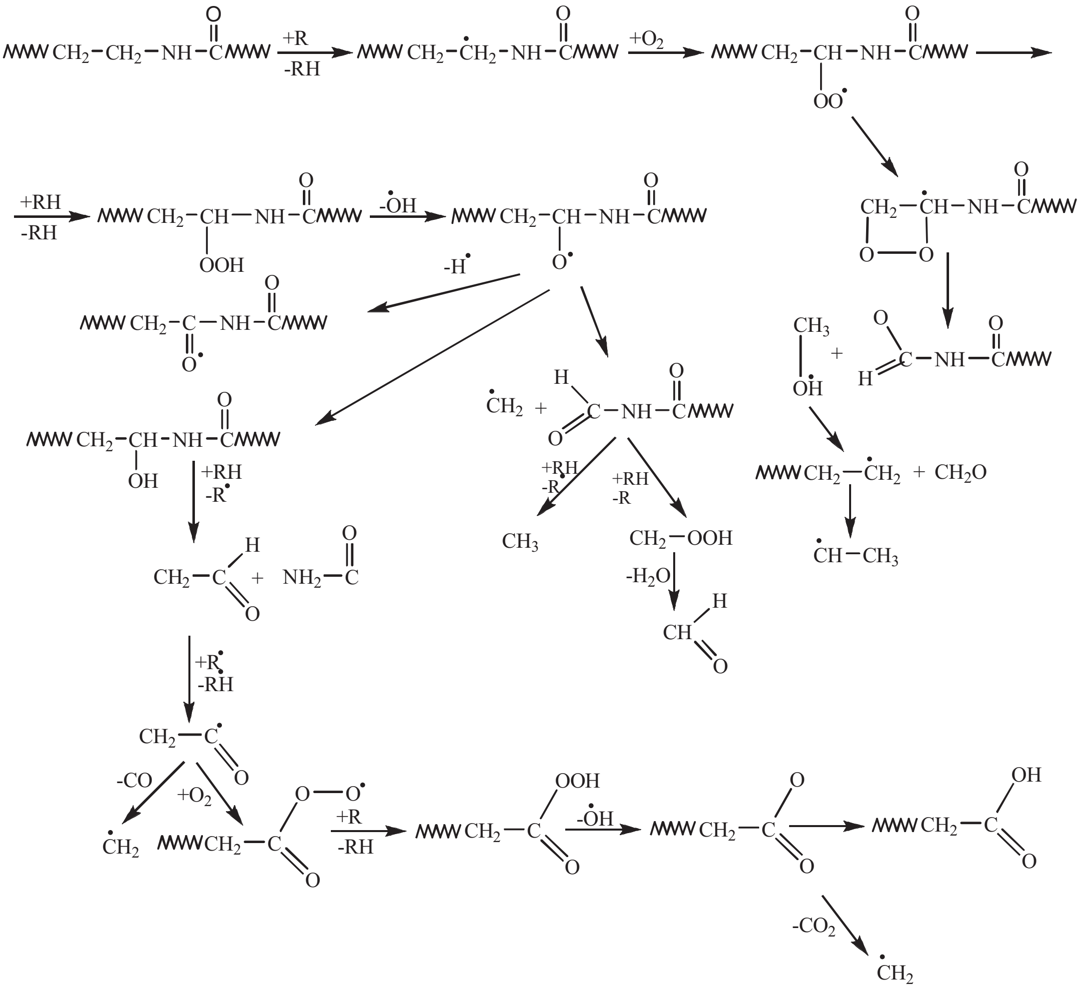

Scheme 1. Thermo-oxidation route according to Karstens and Rossbach [6,7].

further purification. Double distilled water was used throughout the experiments.

LMO was prepared according to the redox method described in [19]. Accordingly, firstly 2 M (mol/L) H_2O_2 and 0.6 M (mol/L) NaOH solutions was mixed and stirred in glass beaker. The molar ratio of $NaOH/H_2O_2$ was adjusted as 0.18. After that, immediately manganese solution was poured in to the mixture. During the addition highly vigorus reaction accured. This reaction continued until to run out all of the manganese solution. After completion of bubbles formation, black precipitate was filtered. Obtained soil was put in to the teflon lined autoclave and waited at 140 °C for 16 h in 2 M sodium hydroxide alkaline solution. As a final opretation obtained grey precipitate was filtered and washed with deionized water until to obtain neutralization. Several IR absorption bands were observed at 3412, 1633, 1384, 1066, 622, 602 and 513 cm^{-1}, respectively. Two strong IR bands could be observed around 513 and 602 cm^{-1}, in good agreement with the IR characteristic bands of birnessites [20–24]. The surface area was calculated by the BET (Brunauer–Emmett–Teller) method. The BET surface area (34.24 m^2/g), external surface area (28.56 m^2/g), micropores surface area (5.68 m^2/g), total pore volume (0.169 cm^3/g) and average pore diameter (19.79 nm) results obtained by applying the BET equation to N_2 adsorption at 77 K and Barret–Joymer–Halenda (BJH) equation to N_2 adsorption at 77 K.

2.2. Characterization techniques

Infrared (IR) spectra of the LMO samples were recorded in the region 4000–450 cm^{-1} on a Spectrum-100 FTIR spectrometer. The thermal gravimetric (TG) and differential thermal analyses (DTA) curves were obtained using a PRIS Diamond TG/DTG apparatus under highly pure nitrogen atmosphere. A Tri Star 3000 (Micromeritics, USA) surface analyzer was also used to measure the nitrogen adsorption isotherm at 77 K in the range of relative pressure 10^{-6}–1. The XRD analysis data from the samples were collected using a Rigaku, Miniflex ZD13113 (Japan) diffractometer with Cu Kα radiation (Ni fitler). Surface morphology was studied using a ZEISS Ultraplus model field emission scanning electron microscopy (SEM).

2.3. Thermal degradation of LMO/PA6 composite

The LMO/PA6 composite was prepared by dissolving stoichiometric amounts of PA6 and LMO in formic acid. The mixture was heated at 40 °C until complete dissolution was achieved. The solution was then cast onto a glass substrate followed by a slow evaporation of the formic acid in a fume hood, then in a vacuum oven at room temperature for 48 h. The thermal decomposition studies in the TGA were performed over a temperature range of