Asian Journal of Chemistry; Vol. 24, No. 2 (2012), 481-484

ASIAN JOURNAL OF CHEMISTRY

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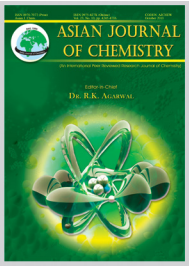

Solvent-Free Synthesis of Phthalimide Under Microwave Irradiation and Modification of Talc with Synthesized Phthalimide

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(*Received*: 13 December 2010; *Accepted*: 3 October 2011) AJC-10465

A simple and effective procedure for the synthesis of phthalimide had been developed under solvent-free microwave irradiation condition and the structure of the synthesized compound had been characterized by FT-IR, ^{1}H NMR. Morphology and thermal properties of phthalimide synthesized by this solvent-free reaction under microwave irradiation were further investigated by scanning electron microscopy (SEM) and TGA thermal analyzer, respectively. SEM showed the particles of phthalimide were not completely regular, but the most of the phthalimide was rodlike and the average length of the rodlike particles was 1 μm. At the same time, the optimized geometric structure of phthalimide was carried out by theoretical calculations using the semiempirical method PM3. The results of TGA indicated that decomposition temperature significantly increased with increasing of heating rate and decomposition rate was fast. Upon heating rate of 10 ºC/min, phthalimide showed good thermal stability of phthalimide under 150 ºC and that the decomposition completed at 250 ºC. Finally, the synthesized phthalimide was used to successfully modify the surface of talc.

Key Words: Phthalimide, Thermal stability, Microwave irradiation, Solvent-free reaction.

INTRODUCTION

Phthalimide is an useful intermediate in organic synthesis and its derivatives had been widely used in synthesis of medicinal chemistry[1-5], organic synthesis[6-9], *etc.* and obtained a lot of progress. Usually, phthalimide is synthesized by carbon dioxide and ammonia method, recycling ammonia, urea method and so on[10]. These methods have limitations such as long time of reaction, environment pollution, low yield[10].

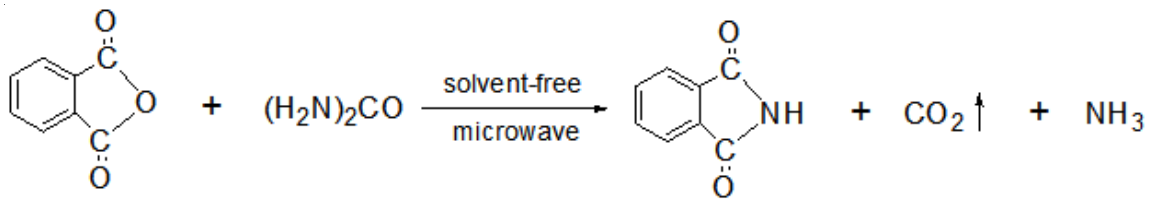
In recent years, microwave irradiation has widely used to simplify and improve organic reactions due to higher yields, cleaner reactions and shorter reaction times compared to conventional heating[11]. For example, many reactions achieved by conventional heating at reflux temperature for many hours can be completed within several minutes or even seconds under microwave irradiation. In connection with solvent-free conditions, microwave irradiation is considered as a green chemistry method. Thus, in this paper, we use this microwave irradiation technology to synthesize phthalimide based on urea and phthalic anhydride and the morphology and thermal properties of the product were further investigated, at the same time, we used this synthesized phthalimide to modify the surface of talc.

EXPERIMENTAL

The materials used in this study were of analytical grade (AR) grade. Urea and phthalic anhydride were procured from Beijing Chemical Reagents Company (Beijing, China) and Chengdu Kelong Chemical Reagents Company respectively (Sichuan Province, China), sodium carbonate was purchased from Mianyang Rongshen Chemical Reagents Company (Sichuan Province, China). Talc was obtained from YueJiang Chemical Reagents Company (Shanghai, China).

Synthesis procedure of phthalimide: Phthalimide was prepared as shown in **Scheme-I**: urea and phthalic anhydride were mixed and the mixture was put into microwave irradiation equipment. After 180 s with 450 W microwave irradiation and cooling to room temperature, obtained crude product was filtrated by water at room temperature and then washed by sodium carbonate solution to eliminate by-products, the resulting product was dried in a vacuum at 45 ºC (yield: 83.5 %).

Modification of the talc with phthalimide: The synthesized phthalimide and talc, in a 1: 9 molar ratio, were mixed and the specific modification process have described in previous literature[12].



Scheme-I: Synthesis of phthalimide

Phthalimide tests (attribute): The infrared spectra were measured on Nicolet 380 FT-IR spectrometer, in the range 4000-400 cm^{-1}. The ^1H nuclear magnetic resonance was recorded on Brucker AVANCE 300 spectrometers the solvent was dimethyl sulphoxide. A S4800 scanning electron microscope at 15 kV voltage (Hitachi, Ltd. Japan) was used to determine the size and morphology of the particles. TGA thermal analyzer was performed using a simultaneous thermal analysis Q500 (TA instrument USA) with a heating ramp of 2.5, 5, 10, 20 °C/min under nitrogen flow (50 mL/min) from room temperature to 500 ºC.

RESULTS AND DISCUSSION

Structures of phthalimide: The FT-IR spectra of phthalimide was shown in Fig. 1. In the spectra, the intense peaks at 3201.9 and 715.8 cm^{-1} contribute to the absorption of N-H stretching vibration and the bending vibration; Owing to vibronic coupling of carbonyl, the absorption peak at 1773.8 and 1739.7 cm^{-1} contribute to C=O stretching vibration. Then the absorption peaks at 1603.7 cm^{-1}, 1463.8 cm^{-1} proved the existence of benzene. The absorption peak at 1306.9 cm^{-1} was C-N stretching vibration peak; the absorption peak at 1138 and 1070.1 cm^{-1} belongs to C-H plane deformation vibration of benzene. Infrared spectrum analysis confirm the synthesis of phthalimide.

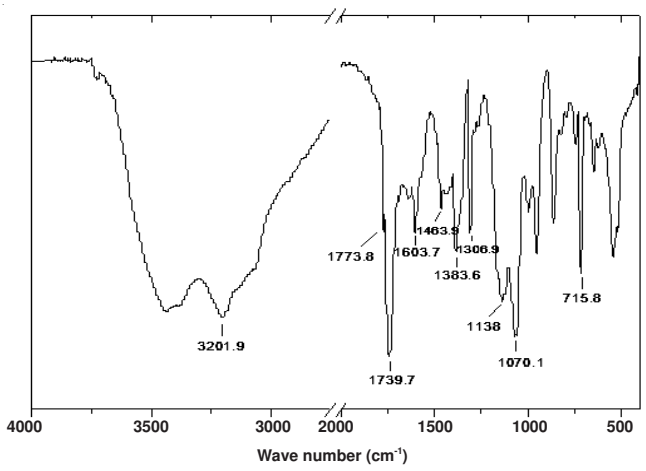


Fig. 1. FTIR spectra of phthalimide

^1H NMR pattern of phthalimide was depicted in Fig. 2. The dot denotes the peaks ascribed to dimethyl sulfoxide as solvent. The single peak at $\delta_H = 11.31$ was N-H proton resonance peak and the other single peak at $\delta_H = 7.82$ was proton resonance peaks of benzene. ^1H NMR analysis further confirmed that phthalimide was successfully synthesized.

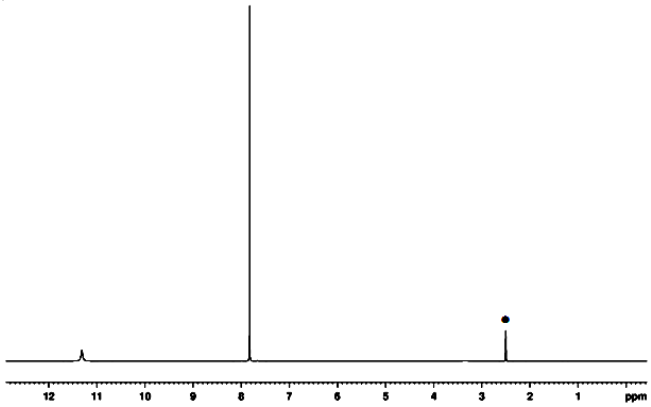


Fig. 2. ^1H NMR spectra of phthalimide

Morphology and geometry optimization of phthalimide: Fig. 3 is SEM images of the synthesized phthalimide particles (B is the partly amplificatory images of A, respectively). The SEM image showed that the particles of phthalimide were not completely regular, resulting from difficulty control of morphology of phthalimide under microwave irradiation. From Fig. 3B, the morphology of most phthalimide was rodlike and the average length of the rodlike particles was 1 μm. In order to further investigate the structure of phthalimide, the optimized geometric structure of phthalimide was carried out by the theoretical calculation and the calculations were performed with the program VAMP using the semiempirical method PM3. The optimized geometry structure of phthalimide is shown in Fig. 4 and the HOMO and LUMO of phthalimide is -9.635 eV and -1.877 eV, respectively.

Thermal stability of phthalimide: Fig. 5 shows the TGA curves of phthalimide with a heating ramp of 2.5, 5, 10, 20 °C/min under nitrogen flow from room temperature to 500 °C. As seen in Fig. 5, there existed only a platform on TGA curves, which indicate that the thermal decomposition of phthalimide is one-step reaction. Meantime, decomposition temperature significantly increased with increasing of heating rate, the reason is that rapid heating rate make decomposition of phthalimide not achieve at set temperature, at the same time, the temperature has get into the following set temperature, resulting in decomposition achieving at higher temperature. As shown in Fig. 5, the decomposition rate was fast during heating. Upon heating rate of 10 °C/min, phthalimide shows good thermal stability of phthalimide under 150 °C and that the decomposition completed at 250 °C.

Modification of talc with phthalimide: Talc is chemically inert, thus, in order to expand application fields of talc, the modification was carried out to change the nature of the native talc. Fig. 6 shows SEM of talc and modified talc. As observed

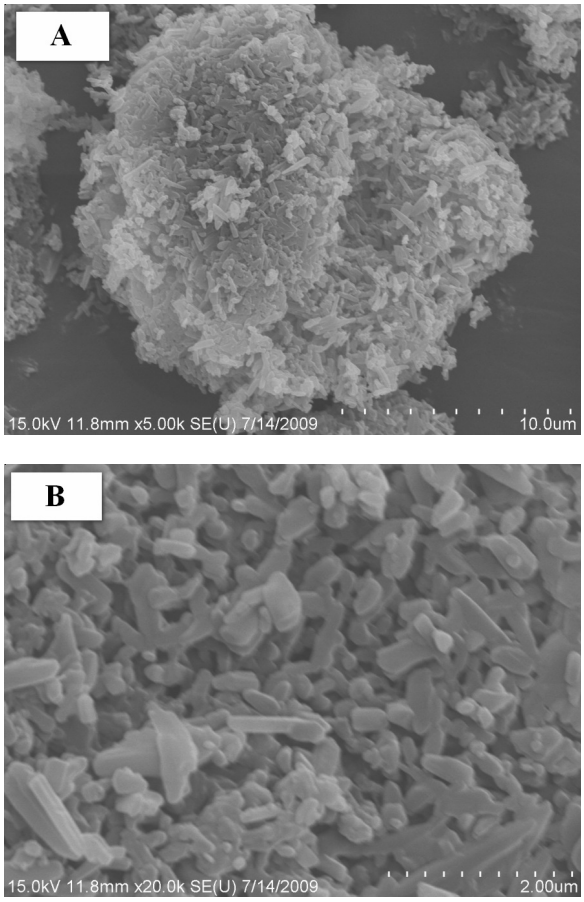


Fig. 3. SEM images of phthalimide

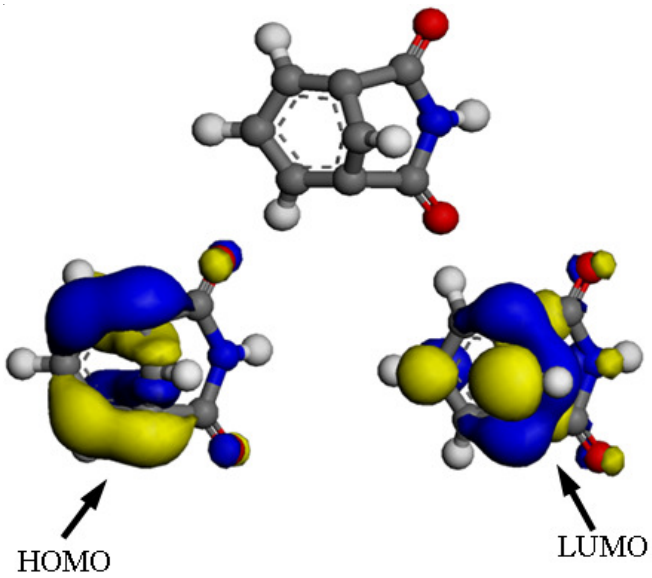


Fig. 4. Optimized geometric structure, HOMO and LUMO of phthalimide

by the SEM, Fig. 1C, the talc is typical layer structure. After modification of talc with phthalimide, the interface between phthalimide and talc become vague, which indicate that the surface of talc was successfully modified with phthalimide and there existed interaction between phthalimide and talc. The interaction may result from a weak bond between the C=O group of the phthalimide and the O-H group of the talc.

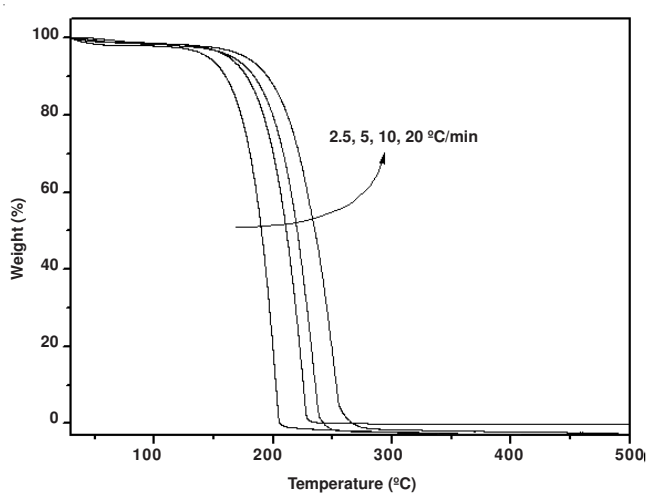


Fig. 5. TGA curves of phthalimide

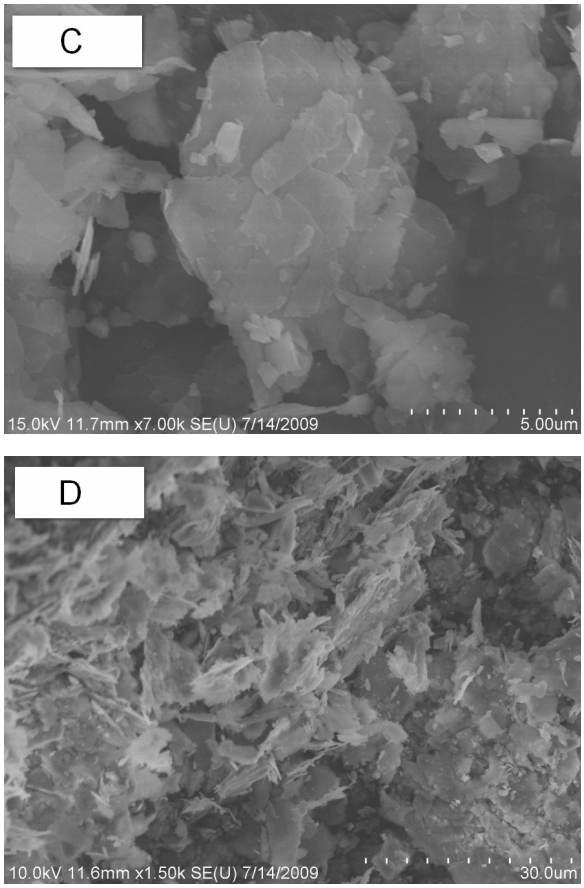


Fig. 6. SEM images of talc (C) and modified talc (D)

Conclusion

Phthalimide was simply and effectively synthesized from urea and phthalic anhydride by solvent-free reaction using microwave irradiation. SEM of phthalimide showed the most phthalimide was rodlike, the average length of the rodlike particles was 1 μm. The thermal stability of the phthalimide showed that the decomposition temperature significantly increased with increasing of heating rate and decomposition rate was fast during heating. Upon heating rate of 10 °C/min, phthalimide showed good thermal stability of phthalimide

under 150 °C and that the decomposition completed at 250 °C. The modification of the surface of talc was successfully carried out with the synthesized phthalimide and there existed a weak bond between the C=O group of the phthalimide and the O-H group of the talc.

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