PROCEEDINGS

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The 2nd International Seminar on Industrial Explosive Materials

Edited by:The Society of Industrial Explosive Materials of China

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THE PUBLISHING HOUSE OF ORDNANCE INDUSTRY

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《The 2nd International Seminar on Industrial Explosive Materials》

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FORWARD

Five years ago, the International Seminar on Industrial Explosive Materials was held in Nanjing for the first time. This year, we have the honor to join our symposium to the 2nd International Seminar. It is truly a great pleasure for us to be able to convene the assembly of so many distinguished guests from a number of countries. I firmly believe that this meeting should be a successful international event in the field of industrials explosive materials.

The aim of the symposium is to provide an up-to-data comprehensive assessment of recent progress concerning industrial explosive materials. I sincerely hope that, as a consequence of the seminar, the cooperations between scientists and engineers who share the common interest in industrial explosive materials will be strengthened.

Collected in this proceedings are 81 papers accepted for presentation at this Seminar. More than 200 authors and co-authors all over the world contribute to them. These papers cover the following aspects: industrial explosives, detonators, fuses, blasting materials used in oil(gas)well, epicenter materials, pyrotechnics materials and initiating devices, new blasting techniques and their related safety techniques, the manufacturing method, theoretical investigation, measuring, application of the above device or materials, and so on.

As the chairman of the Seminar, I would like to extend my hearty appreciation to the sponsors, the Society of Industrial Explosive Materials of China and China Institute of Industrial Explosive Materials for all they have done for this meeting. Meanwhile, welcome to attending this seminar and wish all of you have a fruitful and successful meeting and an enjoyable stay in Nanjing.

Zhang Weimin
Chairman of the 2nd International Seminar on Industrial Explosive Materials
Nanjing

Contents

SECTION Ⅰ

Basic Theory

Preparation and Catalysis of CNTs/PMMA Composite Particles

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Abstract In order to modify the using performance of carbon nanotube in solid propellants of rocket, we coated the carbon nanotube by the Poly(methyl methacrylate)(PMMA), and characterized by TEM, FT-IR. To analyze the catalytic effect of CNTs/PMMA composite particles on the thermal decomposition of AP, the comparison samples by pure AP, simply mixing CNTs with AP respectively have been prepared, CNTs/PMMA/AP composite particles prepared by a novel solvent evaporation method and DTA experiments were used to characterize their catalytic performance. It is shown that CNTs/PMMA have the catalytic performance and the CNTs in the composite particles exhibit the better catalytic performance on the thermal decomposition of AP. Compared with the sample of pure AP, the peak temperature of high temperature decomposition of CNTs/PMMA composite particles decreases 113. 9℃, and the total heat release improves from 309. 92～984. 18 J/g, and the simply mixing sample is 709. 50 J/g. It is shown that the catalytic performance of CNTs on the thermal decomposition of AP can be improved by composition with PMMA, and we also find that the CNTs/PMMA/AP composite particles exhibit the best catalytic performance on the thermal decomposition of AP, compared with the sample of CNTs/PMMA, the peak temperature of high temperature decomposition of CNTs/PMMA/AP composite particles decreases 7. 8℃, and the total heat release improves 114. 29J/g.

Keywords carbon nanotube, PMMA, composite particle, ammonium perchlorate, catalytic performance

1 Introduction

As known, AP is often used in solid propellants of rocket as oxidizing agent. AP is 70%(*wt*)in the AP propellants. Its unique peculiarity has great effect on the whole function of solid prop ellants of rocket. Particularly, the burning ability relates closely with the thermal decomposition of AP[1]. Because the diameter of nanocatalyst is very small, and very larger surface area compared to its quality. The microstructure of crystal particle has a lot of lattice defects. So its reaction activity is very well, and added nanocatalyst can make its burning ability better[2]. Since the first pioneering report of the discovery of CNTs by expert Iijima in 1991[3], carbon nanomaterials have drawn great attention throughout the world. As the burning rate additive of solid propellants of rocket, the quality of CNTs is better than carbon black[4～5]. As another allotropic form of carbon, CNTs will be the important material in the solid propellants of rocket due to their unique mechanical and thermal properties. But nanoparticles are prone to coacervate, and they can not be mixed with the other materials of propellants very well. So this effects its application. PMMA is often used in propellants as adhesive. PMMA are also used to modify the using performance of CNTs and that makes CNTs disperse well. In order to increase their contact area, we compound CNTs with AP; we want to

find better catalytic performance on the thermal decomposition of AP.

2 Experiments

2.1 Apparatus and reagents

Benzene, thiophene, ferrocene, absolute ethylalcohol, deionized water, concentrated sulfuric acid concentrated nitric acid, PMMA, methey benzene, AP(Dalian potassium chlorate company). Japan H-600 TEM and Infra-red spectroscopy(Canada Boman154s) were employed. Compound particles were measured with a differential thermal analysis of Japan Shimadzu company, at a heating rate of 20℃/min.

2.2 Preparation of compound particles

2.2.1 Preparation and purification of CNTs

Benzene was used as carbon source, thiophene as promoter for the grown of CNTs, ferrocene as catalyst. At 1100～1220℃, hydrogen was used as carrier gas to carry the mixture which consisted of benzene and thiophene, and then held for 30 min, at last cooled back to room temperature at the protection of Ar. Then CNTs were found. In order to remove the catalytic particles, nonfixed form carbon and other impurities, the CNTs can be purified by a purification procedure in which a sequence of steps including HNO_3 and HCL washing, then passed a cooler at 100℃ for 2 h. Distilled water washing was employed to make it become neutral.

2.2.2 Preparation of CNTs/PMMA composite particles

Some PMMA and 10mL methyl benzene were added to three flasks. When PMMA dissolved, added 10mL absolute ethylalcohol, continued mixing until they formed emulsion. At last, CNTs was put in, heated at 80℃ in order to make solvent evaporated. Then dried and measured.

2.2.3 Preparation of CNTs/PMMA/AP composite particles

CNTs/PMMA composite particles and AP were mixed at the function of supersonic wave. They would dispersed averagely in the mixture which made of water and absolute ethylalcohol, then heated at 80℃ and mixed. Then AP would decompose on the surface of the CNTs/PMMA composite particles. After that, they were taken out and dried.

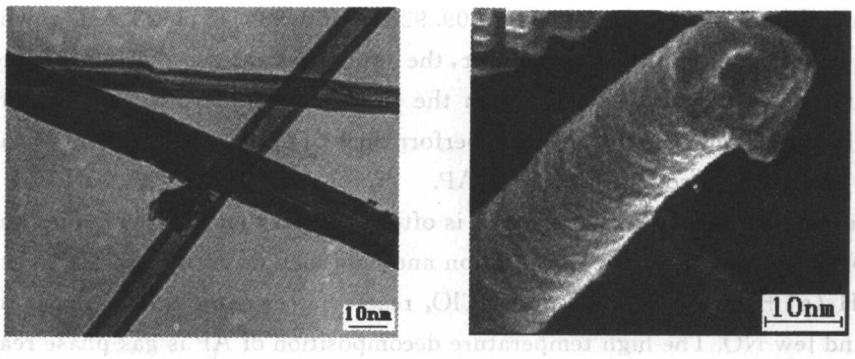
3 Results and discussion

3.1 Characterization of CNTS/PMMA composite by TEM

The following two TEM images show the surface of CNTs and CNTs/PMMA particles. In the present study, the prepared CNTs have a lot of impurities. These impurities hinder the application of CNTs. When the CNTs purified by acid, the CNTs are very pure and their surfaces are smooth now, the diameter is 10nm. But when modified by the PMMA, the surfaces of CNTs are very rough and there is some bamboo-like of black fiber-like materials in CNTs. The surfaces of CNTs are oleophylic, so the PMMA are prone to combine with CNTs in the emulsion, and then form coating structure(Fig. 1).

3.2 Analysis of infra-red spectroscopy

From the FI-IR patterns of different samples, a hydroxyl group peak can be seen at ca. 1720 cm^{-1} (curve line b), and a weak peak can be seen at ca. 3400cm^{-1}. At high temperature, the surface carboxyl group peak of CNTs become weak which is due to the concentrated nitric acid spilt into NO_2 and [O], and then [O] will combined with carbon that they formed ketone group on the surface of CNTs[6]. At last, ketone group with hydroxyl group formed carboxyl group. Curve line b compared with curve line c, a strong hydroxyl group



(a) (b)

Fig. 1 TEM images of carbon nanotubes purified by acid(a) and CNTs/PMMA composite particles(b)

absorbing peak can be seen at ca. 3400cm^{-1} (CNTs/PMMA composite particles) and disappeared at ca. 1720cm^{-1}. A C-H vibration peak can be seen near ca. 1120cm^{-1} which shows the composite particles contain PMMA (Fig. 2).

3.3 Effect of CNTs/PMMA on thermal decomposition of AP

Samples AP, CNTs/AP, mixture which consisted of same quality of CNTs and AP, and CNTs/PMMA/AP composite particles(signed a-d) were measured. The DTA patterns of samples a, b and c show that AP DTA pattern has one absorbing peak and two releasing heat peak. The absorbing heat peak at 248℃ shows that AP transforms form rhombic lattice to cubic lattice. The low temperature decomposition of AP is showed by the releasing heat peak at 362.8℃. AP partly becomes intermediate product. AP complete decomposed to volatile matters. When added CNTs particles, the peak temperature of high temperature decomposition of AP coincides with it peak temperature of low temperature decomposition in range 280～412℃. But the peak temperature of high temperature decomposition of CNTs/PMMA composite particles decreases 113.9℃, the peak of low temperature decomposition is disappeared. It is shown that the catalytic performance of CNTs on the thermal decomposition of AP can be improved by composition with PMMA. From curve lines a and d, the peak temperature of high temperature decomposition of AP in CNTs/PMMA/AP composite particles decreases 121.7℃. Form curve lines c and d, compared with the sample of CNTs/PMMA, the peak temperature of high temperature decomposition of CNTs/PMMA/AP composite particles decreases 7.8℃ (Fig. 3).

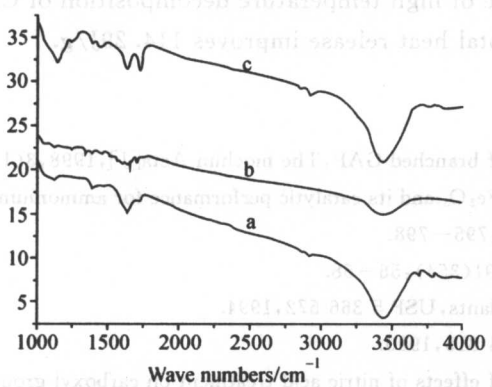


Fig. 2 FT-IR patterns of carbon nanotube and CNTs/PMMA extracted by toluene
a—original sample of carbon nanotubes;
b—carbon nanotube purified by acid;
c—CNTs/PMMA composite particles

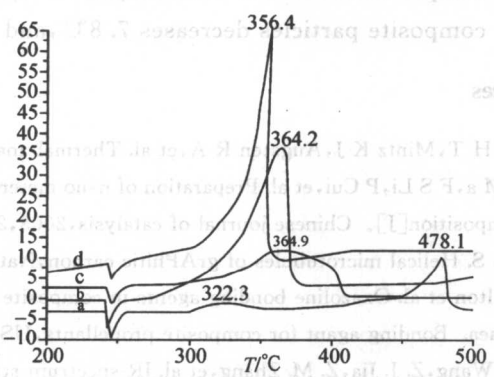


Fig. 3 DTA patterns of different samples
a—AP; b—CNTs, AP;
c—CNTs/PMMA composite particles and AP;
d—CNTs/PMMA/AP composite particles

The total heat releases of four samples are 309.92, 709.50, 984.18, 1128.47J/g. when the peak temperature of high temperature decomposition lower, the total heat release more lager and concentrated. It shows that the catalytic performance of CNTs on the thermal decomposition of AP can be improved by composition with PMMA. And that the catalytic performance of CNTs/PMMA on the thermal decomposition of AP can be improved by composition with AP.

The thermal decomposition mechanism of AP is often thought that the low temperature decomposition is solid-gas heterogeneous reaction. The dissociation and sublimation process is: $NH_4^+ + ClO_4^- = NH_3(s) + HClO_4(s) = NH_3(g) + HClO_4(g)$, NH_3 and $HClO_4$ reacted after entering gas-phase, the product are N_2O, O_2, Cl_2, H_2O and few NO. The high temperature decomposition of AP is gas-phase reaction, the product are NO, O_2, Cl_2 and H_2O[7-8]. It is shown that CNTs and CNTs in the composite particles exhibit the better catalytic performance on the thermal decomposition of AP. Because of the opening structure of CNTs, the gas product of AP are absorbed directly by the active site of catalyst, it makes active center of catalyst prone to react. But CNTs can be dispersed well in AP. And this affects its catalytic performance. The coating films of CNTs are very thin, and the percentage of quality is small. Compared with AP, its decomposition temperature is lower than AP. So it can not effect the thermal decomposition of AP. But when compounded, it can increase the contact area with AP, that the catalytic performance of CNTs on thermal decomposed of AP can be improved.

4 Conclusions

(1)CNTs/PMMA composite particles have been successfully synthesized. The TG analysis shows that PMMA was 36.51%(*wt*) in the CNTs/PMMA composite particles. It is shown that CNTs/PMMA have the catalytic performance and the CNTs in the composite particles exhibit the better catalytic performance on the thermal decomposition of AP. Compared with the sample of pure AP, the peak temperature of high temperature decomposition of CNTs/PMMA composite particles decreases 113.9℃, and the total heat release improves from 309.92～984.18 J/g, and the simply mixing sample is 709.50J/g.

(2)CNTs/PMMA/AP composite particles prepared by a novel solvent evaporation method and DTA experiments were used to characterize their catalytic performance. we also find that the CNTs/PMMA/AP composite particles exhibit the best catalytic performance on the thermal decomposition of AP, compared with the sample of CNTs/PMMA, the peak temperature of high temperature decomposition of CNTs/PMMA/AP composite particles decreases 7.8℃, and the total heat release improves 114.29J/g.

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Clean Mononitration of Toluene in Novel Brønsted Ionic Liquid

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Abstract Novel Brønsted ionic liquid 1-metyl-3-propanesulfonic acid immidazolium hydrogen sulfate($MIMPSHSO_4$) has been prepared as catalyst for the greener chemical processes of nitration reaction. Nitration reaction carried out for 10h at 60℃ with a catalyst to reactant molar ratio of 0.02, the yield of mononitration was 70%, and selectivity of mononitration was 100% with a para to ortho ratio of 0.7. Biphasic system of product and catalyst was obtained and the product could be separated simply by decantation. In addition, ionic liquid could be recovered and reused showing the possibility of a clean chemical process.

Keywords ionic liquid; clean nitraton; toluene

1 Introduction

Electrophilic nitration of toluene is an immensely important and widely studied chemical reaction owing to its useful products, which are used as key organic intermediates or energetic materials. The mechanistic and synthetic aspects of nitration reaction have been very thoroughly studied over the years.[1] Unfortunately, the usual commercial process is not environmentally benign since it results in disposal problems, necessitates regeneration of used acids, and often provides poor selectivity for the desired products. The concept of recoverable and recyclable catalysts has become extremely important from both the environmental and economical points of view. In these years, there is a growing interest in the development of the greener chemical processes that do not lead to three major sources of waste. Various nitration approaches have therefore been explored in order to avoid the problems of the traditional mixed acid method, which uses nitric and sulfuric acids. The new approaches particularly involve the use of recyclable catalysts such as lanthanide triflates or solid acid catalysts such as perfluorinated resin sulfonic acid, calycop and zeolites.[2-5] Although much success has been achieved, some problems still exist. For example, the use of lanthanide triflates or polymeric sulfonic acid resins as catalysts does not improve the selectivity, and furthermore, chlorinated solvents are required in the former process. Solid acids are nonvolatile materials and benign to environment but have shortcomings such as high molecular weight/active-site ratios and rapid deactivation from coking. In the processes of employing zeolites as catalysts, the byproducts, water, or other small molecules formed during the reaction can block the pores of the zeolite and deactivate the catalyst.

In recent years, air- and water-stable room-temperature ionic liquids(RTILs) have emerged as a powerful alternative to conventional molecular organic solvents due to their particular properties, such as undetectable vapor pressure, wide liquid range, as well as ease of recovery and reuse, and making RTILs a greener alternative to volatile organic solvents. Rajagopal and Srinivesan[6] investigated nitration of phenol using iron nitrate. Lancaster and Liopis-Mestee [7] studied several nitration systems and they demonstrated that HNO_3/Ac_2O was their best system. Laali and Gettwert [8] investigated the nitration of various substrates,