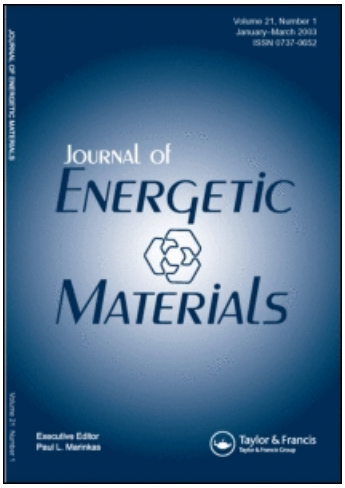

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Approach to the Catalytic Mechanism of Fullerene in Propellants

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Through burning rate experiments and thermal analysis, the influence of adding three forms of carbon—carbon black, C_{60}, and fullerene soot—separately in double-based propellants is studied. It is shown that C_{60} and fullerene soot enhance the burning rate of double-based propellants and broaden the plateau region. By the AM1 method calculation, an attractive force between C_{60} and NO is proved, which suggests a catalytic effect of fullerene on NO reduction, in contrast with a repellent force between graphite structure and NO. From analysis of the molecular structure of fullerene and its bonding ability, the catalytic mechanism of Pb_xC_{60} active sites is posed to explain why C_{60} and fullerene soot have better catalytic effects than carbon black in a Pb-Cu-carbon black catalytic system in double-based propellants.

Keywords: propellants, fullerene soot, C_{60}, carbon black, catalytic mechanism, AM1 method

Introduction

When double-based propellants are burned and decomposed, a great amount of nitric oxide, nitrogen dioxide, and nitrogen monoxide is released, which pollutes the air severely. It is shown [1] that NO_x is

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approximately 38.4% in the gas produced by double-based propellant decomposition. Experiments [2] have demonstrated that small amount of added carbon increases the catalytic effect of lead salts on NO_x reduction, therefore enhancing the burning rate of propellants. Commonly, carbon black is used in double-based propellants as a catalyst. With the development of fullerene preparation, low-priced fullerenes are now available. We have explored adding fullerenes instead of carbon black into double-based propellants and got positive results [3]. D. A. Feikema has done a similar exploration [4]. The combustion process of propellants is greatly affected when fullerenes are used instead of carbon black as the additive. This article discusses the catalytic effects and mechanism of fullerene soot and C_{60} in the combustions of double-based propellants, compared with carbon black. It can be anticipated that fullerenes will have a brighter future in the catalysis area of propellants.

Experiments

Sample

Four kinds of samples of RDX-CMDB double-based propellants were prepared, which contain 2.5% lead salts and 0.4% copper salts. The first sample (C1) contains no carbon, whereas the other three samples (C2, C3, and C4) were separately added with three different forms of carbon (0.3%): fullerene soot, C_{60}, and carbon black. In this article, C_{60} refers to the extractable fullerenes in which C_{60} is dominant, and fullerene soot was prepared by the discharge of a carbon arc and contained 10% C_{60}.

The Burning Rate and Thermal Decomposition Experiments

The burning rate curves were obtained when the four samples were burned under pressure ranging from 2 to 22 MPa. The plateau region as well as burning rates is shown in Table 1. The total heat releases of the four samples obtained by DSC measurements (in nitrogen atmosphere, heat rate 10°C/min) are also shown.

From Table 1, it can be seen that sample C2 has the widest plateau region at 10 MPa and the highest burning rate with 13.05 mm/s, followed by samples C3 and C4. Sample C1 has the lowest burning rate. It also shows that the total heat releases of samples C2 and C3 are greater than those of C1 and C4.

Table 1
Plateau region of burning rate and heat release of the samples

	Sample			
	C1	C2	C3	C4
Plateau region (MPa)	4–10	6–16	8–14	6–12
Width of plateau (MPa)	6	10	6	6
Burning rate on plateau (mm/s)	9.39	13.05	11.08	10.51
Total heat release (J/g)	2788	2937	3026	2843

C1–no carbon, C2–fullerene soot, C3–C_{60}, C4–carbon black.

The Quenched Surface of Propellants

An SEM micrograph shows that the topographic image of samples C2 and C3 is similar and very much different from C4. An EDAX (Pb map) shows that lead in samples C2 and C3 is uniformly and finely dispersed, whereas lead in sample C4 is present as blobs.

Result Analysis

Structural Characteristics and Chemical Properties of Fullerene Soot, C_{60}, and Carbon Black

The characteristic structure of fullerene soot is complicated to analyze. Its ESR spectrum suggests that it contains radicals, which are probably broken or dangling bonds buried deeply inside a protective carbon overcoat [5]. Kroto supposed [6] that fullerene-like structures (not the closed cages like C_{60} or C_{70}) are the ''nuclei'' for roughly spherical soot particles, and incompletely closed fullerene shells are formed to coat the ''nuclei.'' It is also demonstrated that fullerene soot contains 10% C_{60}, which mainly exists as small molecular clusters [7].

C_{60} molecules have a closed ball-like structure, and they are bonded together weakly only through van der Waals forces, although the chemical bonding between carbon atoms within C_{60} is very strong. Compared with them, the surface of carbon black particles is several layers of graphite plane.

From the comparison of the above three carbon forms, we can see that the fullerene soot particle and C_{60} molecule are curved by the incorporation of five-membered rings, whereas carbon black surface

mainly consists of graphite structure (six-membered rings). Hückel molecular orbital calculations show that the presence of the five-membered rings among the six-membered rings in C_{60} gives a LUMO with a triply degenerate t_{1u} state that can accept electrons, whereas the stable HOMO of C_{60} is an h_u level and contains 12 electrons, from which it is difficult to remove electrons [8]. This suggests that C_{60} has high intrinsic activity for reactions with electron donors.

Interaction of C_{60} and NO by AM1 Method Analysis

Research has been done on the reduction of nitric oxide by C_{60}, fullerene soot, graphite, and microporous carbons by Tsang et al., who found that fullerene soot and C_{60} are more active toward oxidation by NO than by oxygen gas at low temperatures (300–400 °C). In contrast, conventional carbons such as graphite and microporous carbons are more readily oxidized by oxygen than by NO [9].

$$x\mathrm{NO} + \mathrm{C} \rightarrow \mathrm{CO}_x + x/2\mathrm{N}_2 \quad (x = 1,\ 2).$$

We believe that the activity of fullerenes is attributed to their five-membered rings to some extent, which are not observed in conventional carbons. From the analysis above, there is a high probability that C_{60} will capture an electron if an electron donor is nearby. Considering the NO molecule as an electron donor and as a major gaseous product on the burning surface, analysis is necessary to figure out the interaction between C_{60} and NO. The computational results by the AM1 program (Austin model 1, a semi-empirical quantum chemistry method [10]) in the Gaussian 94 software package show there is attraction between NO and C_{60}, in contrast with repellence between NO and the graphite plane structure (the main structure of carbon black). To accommodate analysis, NO is separately directed perpendicular to the center of a pentagon (five-membered ring) of C_{60} and to the center of a hexagon (six-membered ring) of a layer of the graphite plane, with the C_s axis of NO vertical to the plane of a pentagon or a hexagon. The system energy changes (ΔE) are shown in Table 2.

In Table 2 the graphite plane structure repels the NO molecule, regardless of NO molecule orientation. Contrasted to it, the system energy of C_{60} and the NO molecule is in a steady decrease from $d = 1.0$ nm to $d = 0.6$ nm, indicating an attractive force. Especially

Table 2
Relative system energy change according to AM1 calculation normalized to $\Delta E = 0$ at $d = 1\,nm$

	d (nm)							
	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
ΔE (10^{-3} eV) C_{60}-ON system	76.5136	4.44992	−0.16048	−0.17952	−0.08160	−0.03536	−0.01360	0.0
ΔE (10^{-3} eV) C_{60}-NO system	−652.3322	5.15440	0.11424	−0.0544	−0.02448	−0.00816	−0.00262	0.0
ΔE (10^{-3} eV) Graphite-ON system	85.85952	7.39296	2.08352	1.66192	1.24304	0.77248	0.34816	0.0
ΔE (10^{-3} eV) Graphite-NO system	56.57328	6.94416	1.47968	1.18864	0.91664	0.57936	0.26112	0.0

d: The distance from the center of a pentagon or a hexagon to the nearer atom side of NO.
C_{60}-ON: O atom of NO attacks a pentagon of C_{60}; others are similar.
In a C_{60} molecule, bond length of C=C is 0.1391 nm, bond length of C-C is 0.1455 nm.
In graphite structure, bond length of C-C is 0.142 nm.

when a N atom of NO attacks a pentagon of C_{60}, the system energy reaches its minimum (a sharp decline) at the distance of 0.3 nm. This demonstrates that a chemical bond is formed. We suppose that a single electron of a N atom has transferred from NO (electron donor) to the LUMO of C_{60} (electron acceptor), and then the resulting NO^+ will be adsorbed to the carbon to continue further reaction.

Pb_xC_{60} Active Sites Catalyze Decomposition of NC and NG

From the results of Table 1, it is evident that fullerene soot and C_{60} as additives enhance the burning rate and broaden the plateau region significantly, which is attributed to the increased decomposition rate of NC and NG [3]. When the double-based propellants are burning, the surface temperature enables the fullerenes (C_{60} as an example) to appear as a single molecule or small molecular clusters. Those fullerenes attach to lead particles to form Pb_xC_{60} catalytic sites, which prevent the coagulation of Pb and PbO and thus improve catalytic activity of lead particles. The research group of S.D. Leifer reported the synthesis of thin films of C_{60} doped with Pb, and the compound Pb_xC_{60} is highly active [11]. So the assumption of Pb_xC_{60} active sites on the burning surface sounds plausible. Considering the converting temperature of C_{60} to amorphous carbon is above 800 °C [12], C_{60} won't decompose on the burning surface of double-based propellants. As an absorbent, C_{60} attracts small molecules, such as NO_2 and HCHO (the decomposed products of NC and NG), to the Pb_xC_{60} active sites, accelerating the following exothermic reactions catalyzed by lead:

$$Pb + NO_2 \rightarrow PbO + NO,$$
$$HCHO + PbO \rightarrow Pb + H_2 + CO_2.$$

With increased heat release on the decomposing surface, the burning rate of propellants is raised subsequently. Combustion characteristics of sample C2 are more improved than those of sample C3, mainly because of the highly active fullerene radicals in fullerene soot, which are more favorable to catalyzing the reactions on the burning surface.

It can be imagined that the temperature of the burning surface in the initial stage is relatively low, and a great number of highly active carbon radicals emerge on the surface as a result of incomplete oxidation of aldehyde catalyzed by Pb_xC_{60}. These radicals are probably absorbed to the surface of fullerenes, together with NO produced

simultaneously. Violent exothermic reactions can occur, which release a great amount of heat:

$$\mathrm{NO + C \rightarrow CO + 1/2N_2} \qquad \Delta H = -6.688 \text{ kJ/(g NO)},$$
$$\mathrm{NO + 1/2C \rightarrow 1/2CO_2 + 1/2N_2} \qquad \Delta H = -9.614 \text{ kJ/(g NO)}.$$

Because of the plane structure of the carbon black particle, NO is repelled by carbon black on the burning surface and is easily released into the gas phase; therefore its chance of being reduced in a condensed phase by carbon is reduced. Considering that the burning rate of propellants is mainly determined by the heat release in the condensed phase, fullerenes have better catalytic effect on the reduction of NO than carbon black has, especially at high temperature. This corresponds to the experimental results.

The Effects of Fullerene on the Plateau Region

The burning rate curves of samples C2 and C3 both show a larger plateau region than sample C4 does, and the region moves toward high pressure. It is supposed that the plateau region is the result of dynamic equilibrium between the elimination of carbon due to oxidation and carbon generation by surrounding lead catalysis. Considering the attractive force of fullerenes, newly created carbon on the burning surface doesn't diminish dramatically and therefore removes the mesa effect of double-based propellants.

Summary

Adding small amounts of fullerene soot and C_{60} into double-based propellants enables one to improve the burning rate and promote the combustion efficiency. The concentration of NO_x in the gaseous product decreases, and therefore the pollution to the atmosphere, especially to the upper air, is reduced. Fullerene soot and C_{60} instead of carbon black, as additives to the double-based propellants, will improve the combustion characteristics of the propellants, probably because of the following two main reasons:

1. Compared with carbon black, fullerene soot and C_{60} disperse the lead catalyst more uniformly and finely on the burning surface, and consequently more lead active sites are formed to catalyze the reaction between NO_2 and aldehyde.

2. Fullerenes on the burning surface catalyze the redox reaction of newly created carbon and NO, with a great quantity of heat released.

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