BTATz-Pb 复合物对双基和 RDX-改性双基推进剂的热行为、非等温动力学及燃烧性能的影响

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摘要: 制备了含 3,6-双(1-氢-1,2,3,4-四唑-5-氨基)-1,2,4,5-四嗪(BTATz)铅复合物(LCBTATz)的双基(DB)推进剂和黑索今(RDX)-改性双基(CMDB)推进剂. 采用热重-微商热重法(TG-DTG)及差示扫描量热法(DSC)研究了其热分解行为和非等温分解动力学, 并在此基础上评价了其热安全性. 结果表明, LCBTATz-DB 复合物中在 350–540 K 之间只存在一个放热分解峰, LCBTATz-CMDB 复合物中存在两个连续的放热分解峰, 在 390–540 K 温度范围内, 其机理方程分别为: $f(\alpha)=\alpha^{-1/2}$ 和 $f(\alpha)=2(1-\alpha)^{3/2}$. 计算了热加速分解温度(T_{SADT})、热爆炸临界温度(T_b)、热点火温度(T_{TIT})和绝热至爆炸时间(t_{lad}), 其值分别为: DB001 复合物, $T_{\text{SADT}}=444.50$ K, $T_{\text{TIT}}=453.96$ K, $T_b=471.84$ K; $t_{\text{lad}}=39.36$ s; CMDB100 复合物, $T_{\text{SADT}}=442.38$ K, $T_{\text{TIT}}=452.89$ K, $T_b=464.13$ K, $t_{\text{lad}}=21.3$ s, 并以此来评价化合物的热安全性. 考察了 LCBTATz-DB 以及 LCBTATz-CMDB 的燃烧性能, 结果表明 LCBTATz 是一种高效的双基燃烧催化剂, 在较大的压力范围内可以显著提高燃速并且大幅度降低压力指数. 对于双基推进剂在 2–8 MPa 压力范围内出现了明显的超燃速现象, 8–12 MPa 出现了“麦撒”效应, 对于改性双基推进剂的压力指数降到 0.18.

关键词: 3,6-双(1-氢-1,2,3,4-四唑-5-氨基)-1,2,4,5-四嗪; 铅盐; 双基推进剂; 改性复合双基推进剂; 非等温动力学; 热安全性; 燃烧性能

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Effects of Lead Complex-Based BTATz on Thermal Behaviors, Non-Isothermal Reaction Kinetics and Combustion Properties of DB/RDX-CMDB Propellants

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Abstract: The composite double base (DB)/hexogen (RDX)-modified double base (CMDB) propellants (Nos. DB001 and CMDB100) were prepared with the lead complex of 3,6-bis(1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (LCBTATz), with and without the ballistic modifier. Their thermal behaviors and non-isothermal decomposition reaction kinetics were investigated by thermogravimetry, derivative thermogravimetry (TG-DTG), and differential scanning calorimetry (DSC). For the LCBTATz-DB propellant, there was one

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mass loss stage in the TG curve and one exothermic peak in the DSC curve over the temperature range 350–540 K. For LCBTATz-CMDB, there were two continuous exothermic stages in the TG curve, and only one corresponding exothermic peak in the DSC curve over the range 390–540 K. The exothermal decomposition reaction mechanisms of LCBTATz-DB and LCBTATz-CMDB follow the functions $f(\alpha)=\alpha^{-1/2}$ and $f(\alpha)=2(1-\alpha)^{3/2}$, respectively (α : conversion degree). The self-accelerating decomposition temperatures (T_{SADT}), thermal ignition temperatures (T_{TIT}), critical temperatures of thermal explosion (T_b), adiabatic times-to-explosion (t_{Tlad}), and thermodynamic parameters of activation reaction were calculated, and the thermal safety was evaluated. For DB001, $T_{\text{SADT}}=444.50$ K, $T_{\text{TIT}}=453.96$ K, $T_b=471.84$ K, and $t_{\text{Tlad}}=39.36$ s. For CMDB100, $T_{\text{SADT}}=442.38$ K, $T_{\text{TIT}}=452.89$ K, $T_b=464.13$ K, and $t_{\text{Tlad}}=21.3$ s. As a high-efficiency combustion catalyst, LCBTATz in double-base propellants increases the propulsion rate and reduces the pressure index for larger scale pressures. This makes the DB propellant appear to have a significant super burning effect at 2–8 MPa and a “mesa effect” at 8–12 MPa. Meanwhile, the pressure exponent of the CMDB propellant decreased to 0.18.

Key Words: 3,6-Bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine; Lead salt; Double-base propellant; Composite modified double base propellant; Nonisothermal kinetics; Thermal safety; Combustion property

1 Introduction

3,6-Bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz), a novel energetic material, was synthesized firstly by Hiskey *et al.*¹ at Los Alamos National Laboratory. It was one of the high-nitrogen energetic compounds with an excellent performance, such as high nitrogen content of 79.02%, density of $1.76 \text{ g} \cdot \text{cm}^{-3}$, enthalpy of formation of $883 \text{ kJ} \cdot \text{mol}^{-1}$, and moderate mechanical and thermal sensitivity.^{2–7} Our research group has been involved in a systematic experimental study about the synthesis and purification,⁶ the burning rate measurement,⁸ the quantum chemistry study,⁵ thermal behavior and kinetic investigation of the thermal decomposition processes,⁷ even as a substitute of hexogen (RDX) in the composite modified double base (CMDB) propellant formulation.⁹ Many researches focusing on the BTATz showed that it had a prospect function as a primary component in the high burning rate propellant for the booster rocket motor and the kinetic energy ammunition, and it also could be used in the minimum signature propellant for the smokeless ammunition.^{8,10–11}

Lead salts,^{12–15} oxides¹⁶ or nano-oxides¹⁷ were usually added to the solid propellant as the combustion catalyst. Although the lead compounds could bring about the heavy metal pollution to the surrounding and human health, it was well known that they could improve the solid propellant ballistic properties, i.e., they could increase burning rate and decrease the pressure exponent of the burning rate. So they are extensively used as one of the key ballistic modifiers in solid propellant formulations.¹⁸ Therefore, the study on them had not any significance unless the excellent substitute was developed. In this work, the lead complex of BTATz (LCBTATz) was synthesized and its structure was also characterized. The thermal behaviors, nonisothermal decomposition reaction kinetics, thermal safety, and combustion properties of double-base (DB) propellant containing LCBTATz or composite modified double-base (CMDB) propel-

lant containing catalyst were investigated.

2 Experimental

Caution! Although none of the compounds described herein have exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices.

2.1 Equipment and conditions

The thermogravimetry-derivative thermogravimetry (TG-DTG) and differential scanning calorimetry (DSC) curves under the condition of flowing nitrogen gas (purity, 99.999%; atmospheric pressure) were obtained by using a TA2950 thermal analyzer (TA Co., USA) and a 204HP differential scanning calorimeter (Netzsch Co., Germany). The conditions of TG-DTG were: sample mass, about 1 mg; N_2 flowing rate, $40 \text{ cm}^3 \cdot \text{min}^{-1}$; heating rate (β), $10 \text{ K} \cdot \text{min}^{-1}$. The conditions of DSC analyses were: sample mass, about 1 mg; N_2 flowing rate, $50 \text{ cm}^3 \cdot \text{min}^{-1}$; heating rate, 5, 10, 15, and $20 \text{ K} \cdot \text{min}^{-1}$; furnace pressures, 0.1 MPa; reference sample, $\alpha\text{-Al}_2\text{O}_3$; type of crucible, aluminum pan with apierced lid. The specific heat capacity (C_p , $\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$) was determined with continuous C_p mode on a Micro-DSC III microcalorimeter (Setaram Co., France). Heating rate, $0.15 \text{ K} \cdot \text{min}^{-1}$; sample mass, about 100 mg; atmosphere, N_2 ; reference sample, calcined $\alpha\text{-Al}_2\text{O}_3$. The burning rates of the samples were measured in a strand burner filled with nitrogen at different pressures, and the samples prepared were the $\Phi 5 \text{ mm} \times 100 \text{ mm}$ cylinder strand coated with polyvinyl formal.¹⁹

2.2 Materials

The lead complex of BTATz used in the propellant was carried out as follows: BTATz (provided by Xi'an Modern Chemistry Research Institute, purity, 99.9%, measured by high performance liquid chromatography)⁵ and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (AR grade) with mole ratio of 1:2 were dissolved into DMSO and deionized water, respectively. The mixture was stirred for

Scheme 1 Structure of the title complex

1.5 h at 70 °C. After that, a precipitate was filtered, washed with water repeatedly and dried at 80 °C. Finally, the orange powder was obtained. Anal. Calc. for $C_{12}H_{16}N_{28}O_3Pb$ (%): C 17.20, H 1.81, N 47.32, Pb 23.63. Found: C 17.2, H 1.9, N 46.7, Pb 24.7. IR (KBr, ν/cm^{-1}): 3017, 2863, 1624, 1506, 1438, 1323, 1042, 780, 674.

The chemical structure of the title complex is shown in Scheme 1.

The sample of DB001 used in the experiment was a DB propellant containing LCBTATz composed of 59% (mass fraction) nitrocellulose (NC), 30% nitroglycerin (NG), 8.5% diethyl phthalate (DEP), and other additives, etc. The strand sample composed of 500 g ingredients and 12.5 g LCBTATz, LCBTATz as ballistic modifier was prepared by a solventless DB propellant extrusion technique, including slurry mixing, rolling, and extruding. The control DB propellant without ballistic modifier (No. DB002) was also prepared for the comparison with the sample DB001.

The RDX-CMDB propellant sample of CMDB100 used in the experiment was composite modified double base propellant containing LCBTATz, composed of 38% (mass fraction) nitrocellulose (NC), 28% nitroglycerin (NG), 2.5% LCBTATz, 26% hexogen (RDX), 5% *N*-nitro-dihydroxyethylamine-dinitrate (DINA) and other auxiliary. The strand sample composed of 500 g ingredients and 12.5 g LCBTATz, LCBTATz as ballistic modifier was prepared by a solventless CMDB propellant extrusion technique, including slurry mixing, rolling, and extruding. The control CMDB propellant without ballistic modifier (No. CMDB101) was also prepared for the comparison with the sample CMDB100.^{20–23}

3 Results and discussion

3.1 Thermal behaviors

The TG-DTG curves of DB001 and CMDB100 propellants at the heat rate of $10 \text{ K} \cdot \text{min}^{-1}$ are shown in Figs.1 and 2, and the DSC curves at the heating rate of 5, 10, 15, $20 \text{ K} \cdot \text{min}^{-1}$ are shown in Figs.3 and 4, respectively.

From Fig.1, it can be found that there is only one mass-loss

Fig.1 TG-DTG curves for propellant DB001

Fig.2 TG-DTG curve for propellant CMDB100

Fig.3 DSC curves for propellant DB001

stage in TG curve, corresponding to one invisible exothermic peak in DSC curve. For TG curve, there is a mass loss of about 77% between 380 and 540 K, which is close to the mass (80%) of NG and NC, and it likely attributes to the volatilization and decomposition of NC and decomposition of NG.²⁴

There are two mass loss stages in Fig.2, corresponding to the two continuous exothermic peaks in the DSC curve. The first begins at 390 K and stops at 495 K, witnessing about 61% mass loss, which is close to the total mass (54%) of the nitroglycerine and nitrocellulose mixture in the RDX-CMDB propellant. It can be attributed to the volatilization and decomposition of the NG/NC mixture, corresponding to the invisible peak in the DSC curve (main exothermic stage, Fig.4). The second follows the decomposition of NG/NC process, and stops at 540 K, with 20% mass loss, which belongs to the RDX decom-

Fig.4 DSC curves for propellant CMDB001

position in the RDX-CMDB propellant. Because the decomposition of RDX occurs in succession, the decomposition heats of the two processes overlap each other part.

3.2 Calculation of nonisothermal reaction kinetics

To explore the reaction mechanisms of the main exothermic decomposition processes of the propellants DB001 and CMDB100 and obtain the corresponding kinetic parameters [apparent activation energy (E_a /(kJ·mol⁻¹)), pre-exponential constant (A /s⁻¹) and the most probable kinetic model functions], the DSC curves at the heating rate of 5, 10, 15, and 20 K·min⁻¹ were dealt with mathematic means, and the basic data and temperature data corresponding to the conversion degrees (α) were found and shown in Tables 1 and 2, respectively.

Five integral methods (General integral, MacCallum-Tanner, Šatava-Šesták, Agrawal, Flynn-Wall-Ozawa) and one differential method (Kissinger) were employed.²⁵⁻²⁷ While the values of E_a obtained by Ozawa's method from the isoconversional DSC curves at the heating rate of 5, 10, 15, and 20 K·min⁻¹, the E_a - α curves were shown in Fig.5. It shows that the activation energy changed slightly in the section of 0.20–0.84 (α) for DB001 and 0.22–0.80 (α) for CMDB100, which were properly selected to calculate the nonisothermal reaction kinetics.

Forty-one types of kinetic model functions and the basic data (Table 2) for the propellant were put into the integral and dif-

Table 2 Temperature data for the main exothermic decomposition processes of the propellants DB001 and CMDB100

α	DB001				CMDB100			
	T_g /K	T_{10} /K	T_{15} /K	T_{20} /K	T_g /K	T_{10} /K	T_{15} /K	T_{20} /K
0.02	444.33	448.86	450.78	452.76	458.39	466.47	468.31	472.22
0.06	451.25	456.19	458.75	461.20	460.04	467.94	470.20	474.13
0.10	455.08	460.22	463.21	465.85	461.42	469.22	471.75	475.71
0.14	457.82	463.14	466.49	469.23	462.61	470.37	473.08	477.08
0.18	460.00	465.5	469.10	471.90	463.69	471.42	474.25	478.29
0.22	461.84	467.49	471.25	474.08	464.67	472.39	475.31	479.40
0.26	463.46	469.25	473.11	475.96	465.58	473.30	476.30	480.42
0.30	464.92	470.84	474.77	477.63	466.44	474.17	477.24	481.38
0.34	466.27	472.33	476.29	479.16	467.26	475.00	478.14	482.30
0.38	467.56	473.74	477.73	480.60	468.04	475.81	479.01	483.18
0.42	468.81	475.10	479.11	481.98	468.80	476.60	479.87	484.03
0.46	470.03	476.43	480.45	483.32	469.54	477.38	480.71	484.87
0.50	471.25	477.76	481.77	484.64	470.27	478.15	481.54	485.70
0.54	472.48	479.10	483.11	485.97	470.99	478.92	482.38	486.53
0.58	473.75	480.48	484.47	487.33	471.73	479.69	483.22	487.36
0.62	475.07	481.90	485.88	488.74	472.46	480.49	484.07	488.21
0.66	476.49	483.42	487.36	490.23	473.23	481.33	484.95	489.08
0.70	478.03	485.04	488.94	491.83	474.04	482.20	485.86	489.99
0.74	479.73	486.84	490.68	493.58	474.90	483.14	486.84	490.96
0.78	481.68	488.86	492.62	495.56	475.85	484.17	487.90	492.02
0.82	483.96	491.21	494.87	497.86	476.92	485.33	489.09	493.21
0.86	486.77	494.06	497.57	500.64	478.17	486.69	490.46	494.58
0.90	490.39	497.75	501.01	504.22	479.70	488.34	492.14	496.25
0.94	495.45	503.04	505.91	509.38	481.74	490.52	494.37	498.47
0.98	504.23	512.80	514.96	519.19	485.08	494.13	498.04	502.18
1.00	522.10	533.15	534.95	542.44	491.03	501.50	505.18	509.73

α is the conversion degree of decomposition process. 5, 10, 15, and 20 in the underhorn of T denote different heating rates (K·min⁻¹) of DSC curve.

ferential equations for calculation. The values of E_a , $\lg A$, and the linear correlation coefficient (r) were calculated on computer with the linear least-squares method, and the most probable mechanism function was selected by the better value of r .²⁵⁻²⁷ The results of satisfying the conditions at the same time were the final results as listed in Table 3, and the relevant functions were the reaction mechanism function of the decomposition

Table 1 Basic data for the main exothermic decomposition processes of the propellants DB001 and CMDB100

	β /(K·min ⁻¹)	T_0 /K	T_g /K	T_p /K	$-\Delta H_f$ /(kJ·g ⁻¹)
DB001	5	405.1	449.12	470.00	1.75
	10	411.2	452.84	476.56	1.56
	15	417.8	457.78	480.96	1.85
	20	418.8	461.11	483.65	1.67
$-\Delta H_d$					1.70
CMDB100	5	419.8	449.83	469.94	1.22
	10	420.3	455.53	477.12	0.92
	15	421.3	460.68	480.37	1.02
	20	421.8	463.68	484.79	1.13
$-\Delta H_d$					1.07

T_0 is the initial temperature point at which DSC curve deviates from the base line. T_g is the onset temperature for the main exothermal decomposition reaction in DSC curve and T_p is the peak temperature. $-\Delta H$ is the decomposition heat and $-\Delta H_d$ is enthalpy of formation.

Fig.5 E_a - α curves for the propellants of DB001 and CMDB100
 E_a is the apparent activation energy of kinetic model functions.

Table 3 Kinetic parameters for the main exothermic decomposition process of the propellants DB001 and CMDB100

Method	DB001				CMDB100		
	$\beta/(\text{K} \cdot \text{min}^{-1})$	$E_a/(\text{kJ} \cdot \text{mol}^{-1})$	$\lg(A/\text{s}^{-1})$	r	$E_a/(\text{kJ} \cdot \text{mol}^{-1})$	$\lg(A/\text{s}^{-1})$	r
general integral	5	179.59	17.25	0.9994	184.21	18.47	0.9996
	10	171.42	16.35	0.9994	175.61	17.47	0.9996
	15	176.68	16.95	0.9995	175.10	17.45	0.9996
	20	178.80	17.19	0.9995	178.84	17.80	0.9996
MacCallum-Tanner	5	180.16	17.27	0.9994	184.86	18.51	0.9996
	10	172.04	16.38	0.9994	176.34	17.50	0.9995
	15	177.41	16.98	0.9996	175.90	17.48	0.9997
	20	179.59	17.23	0.9995	179.73	17.86	0.9996
Šatava-Šesták	5	178.28	17.10	0.9994	182.72	18.31	0.9996
	10	170.62	16.26	0.9995	174.68	17.36	0.9995
	15	175.68	16.83	0.9996	174.26	17.33	0.9997
	20	177.74	17.07	0.9995	177.88	17.69	0.9996
Agrawal	5	179.59	17.25	0.9994	184.21	18.47	0.9996
	10	171.42	16.35	0.9994	175.61	17.47	0.9995
	15	176.68	16.95	0.9995	175.10	17.44	0.9996
	20	178.80	17.19	0.9995	186.39	17.80	0.9996
Mean		176.53	16.91	0.9995	178.84	17.77	0.9996
Flynn-Wall-Ozawa		181.08		0.9997	172.18 (Epo)		0.9959
Kissinger		182.50	18.20	0.9997	173.13	17.14	0.9955

A is the pre-exponential constant of kinetic model functions. r is the linear correlation coefficient.

process.

From Table 3, one can see that the values of E_a and $\lg A$ obtained from thenonisothermal DSC curves are approximately in agreement with the values calculated by Kissinger's method and Ozawa's method, and the mechanism function number is determined. The decomposition reaction mechanism functions of two propellants are listed in Table 4. The substituting $f(\alpha)$ expression, and the values of E_a and A into Eq.(1), the corresponding kinetic equations [Eqs.(2) and (3)] of the decomposition reaction of the propellants are obtained and shown in Table 4.

$$d\alpha/dt = Af(\alpha)\exp(E/RT) \quad (1)$$

$$d\alpha/dt = 10^{16.91} \times (\alpha^{-1}/2) \times \exp(-1.76 \times 10^5/RT) \quad (2)$$

$$d\alpha/dt = 10^{17.77} \times 2(1-\alpha)^{3/2} \times \exp(-1.78 \times 10^5/RT) \quad (3)$$

3.3 Thermal safety studies

3.3.1 Self-accelerating decomposition temperature

The values (T_{e0} and T_{p0}) of the onset temperature (T_e) and peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq. (4),²⁵⁻²⁷ are listed in Table 5.

$$T_{(e \text{ or } p)_i} = T_{(e0 \text{ or } p0)} + b\beta + c\beta_i^2, \quad i = 1 - 4 \quad (4)$$

$$T_{e0} = T_{\text{SADT}} \quad (5)$$

where b and c are coefficients, T_{SADT} is the self-accelerating de-

composition temperature.

3.3.2 Thermal ignition temperature (T_{ITT}) and critical temperatures of thermal explosion (T_b)

The corresponding critical temperatures of thermal explosion (T_{be} and T_{bp}) obtained from Eq.(6),²⁸ are also listed in Table 5. The high values of T_b for DB001 and CMDB100 propellants show that the transition from thermal decomposition to thermal explosion is not easy to take place.

$$T_{be \text{ or } bp} = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e0 \text{ or } p0}}}{2R} \quad (6)$$

where R is the gas constant, E_o is the value of E_a by Ozawa's method.

3.3.3 Adiabatic time-to-explosion

The adiabatic time-to-explosion (t_{Tlad}) of energetic materials is the time of decomposition transiting to explosion under the adiabatic conditions and is an important parameter for assessing their thermal stability and safety.

Substituting the following data into Smith equations [Eqs. (7)–(9)],^{29,30} the values of t_{Tlad} for the propellants are acquired and also listed in Table 5.

$$C_p \frac{dT}{dt} = QA \exp(-E/RT)f(\alpha) \quad (7)$$

$$t = \int_0^t dt = \int_{T_0}^T \frac{C_p \exp(E/RT)}{QAf(\alpha)} dT \quad (8)$$

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (9)$$

For the propellant DB001: $C_p = -20.95 + 0.195T - 5.69 \times 10^{-4}T^2 + 5.61 \times 10^{-7}T^3$ ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$), $Q = -\Delta H_d = 1703.5 \text{ J} \cdot \text{g}^{-1}$, $A = A_K = 10^{18.20} \text{ s}^{-1}$, $E = E_K = 182500 \text{ J} \cdot \text{mol}^{-1}$, $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, mechanism $f(\alpha) = \alpha^{-1}/2$, the integral lower limit $T_1 = T_{e0} = 444.5 \text{ K}$, the upper limit $T_2 = T_b = 471.8 \text{ K}$. E_K and A_K are calculated by Kissinger method.

Table 4 Mechanism functions, apparent activation energies, and kinetic equations for the propellants DB001 and CMDB100

Method	DB001 ($\alpha=0.20-0.84$)	CMDB100 ($\alpha=0.22-0.90$)
Mechanism function	$G(\alpha)=\alpha^2, f(\alpha)=\alpha^{-1}/2$	$G(\alpha)=(1-\alpha)^{-1/2}, f(\alpha)=2(1-\alpha)^{3/2}$
Mech funct. No.	27	38
$E_a/(\text{kJ} \cdot \text{mol}^{-1})$	176.53	178.84
Kinetic equation	(2)	(3)

Table 5 Derivative parameters for DB001 and CMDB100

System	T_{SADT}/K	T_{p0}/K	T_{TIT}/K	T_{b}/K	t_{TUD}/s	$\Delta S^\ddagger/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$\Delta H^\ddagger/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta G^\ddagger/(\text{kJ}\cdot\text{mol}^{-1})$
DB001	444.50	461.62	453.96	471.84	39.36	99.87	178.66	132.56
CMDB100	442.38	453.73	452.89	464.13	21.30	79.72	169.36	133.18

Table 6 Burning rates (u) of DB001, DB002, CMDB100, and CMDB101 at different pressures

System	$u/(\text{mm}\cdot\text{s}^{-1})$										
	2 MPa	4 MPa	6 MPa	8 MPa	10 MPa	12 MPa	14 MPa	16 MPa	18 MPa	20 MPa	22 MPa
DB001	6.63	8.13	9.18	9.87	9.65	9.62	10.21	11.23	12.46	13.6	6.63
DB002	2.15	3.59	5.20	6.49	7.81	8.99	9.77	10.38	11.22	12.24	13.38
CMDB100	8.01	9.89	10.65	10.93	11.36	12.22	13.64	15.31	17.05	18.81	8.01
CMDB101	3.09	5.34	7.42	9.85	11.88	14.04	15.75	17.54	19.23	20.92	3.09

For the propellant CMDB100: the specific heat capacity, $C_p=2.60-1.16\times 10^{-2}T+2.49\times 10^{-5}T^2$ ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$), $Q=-\Delta H_a=1072.5\text{ J}\cdot\text{g}^{-1}$, $A=A_k=10^{17.14}\text{ s}^{-1}$, $E=E_k=173130\text{ J}\cdot\text{mol}^{-1}$, $R=8.314\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, mechanism $f(\alpha)=2(1-\alpha)^{3/2}$, the integral lower limit $T_i=T_{\text{co}}=442.4\text{ K}$, the upper limit $T_2=T_b=464.1\text{ K}$.

3.3.4 Thermodynamic parameters of activation reaction

The entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), and free energy of activation ($\Delta G^\ddagger$) of the decomposition reaction, corresponding to $T=T_{\text{p0}}$, $E_a=E_k$, and $A=A_k$, are obtained from Eqs.(10)–(12),^{25,26} respectively, and also listed in Table 5. The positive values of $\Delta G^\ddagger$ indicate that the exothermic decomposition reaction of the propellants must proceed under the heat condition.

$$A=\frac{k_{\text{B}}T}{h}\text{e}^{\Delta S^\ddagger/R} \quad (10)$$

$$\Delta H^\ddagger=E_a-RT \quad (11)$$

$$\Delta G^\ddagger=\Delta H^\ddagger-T\Delta S^\ddagger \quad (12)$$

where k_{B} is the Boltzmann constant, and h is the Plank constant.

From Table 5, the calculated values of T_{SADT} , T_{TIT} , and T_{b} for the propellant DB001 and CMDB100 show that they have the high thermal safety from adiabatic decomposition to explosion.

3.4 Combustion property

For the sake of the possible application of LCBTATz in DB propellant and RDX-CMDB propellant, the burning rates [$u/(\text{mm}\cdot\text{s}^{-1})$] of DB002 (mass fractions of NC/NG/DEP/auxiliary: 59%/30%/8.5%/2.5%) and DB001 were measured under different pressures (p).

Also, the CMDB101 (mass fractions of NC/NG/RDX/auxiliary: 38%/28%/26%/8%) and CMDB100 were measured under

different pressures, respectively. The data are listed in Table 6 and the curves of burning rates are shown in Figs.6 and 7. It can be seen that with the help of the catalysis of LCBTATz, the burning rate of the DB propellant and RDX-CMDB propellant are improved observably. The burning rate of the DB propellant can be improved by 208.4% at 2 MPa and “super burning effect” is occurred at 2–8 MPa, and burning rate of the CMDB propellant can be improved by 159.2% at 2 MPa and the burning rate is increased remarkably at 2–8 MPa.

In order to evaluate the effects of the ballistic modifier on the combustion property of the propellants, the pressure exponent (n) of the burning rate was calculated, and the mean value of the catalysis efficiency ($\bar{Z}$) was compared before and after LCBTATz was added into the propellant formulation. The values of n and $\bar{Z}$ were obtained by Eqs.(13) and (14),^{31,32} and the relationship between Z and test pressure were shown in Figs.8 and 9.

$$u_i=ap_i^n, i=1-11 \quad (13)$$

$$Z=\sum_{i=1}^k(\mu_{\text{IIVII}}/\mu_{\text{IIVII}})/K \quad (14)$$

where, I: without catalysis DB propellant, II: 2.5% LCBTATz DB propellant, III: without catalysis RDX-CMDB propellant, IV: 2.5% LCBTATz RDX-CMDB propellant

For DB001:

at 2–8 MPa, $u=5.41p^{0.289}$, $r=0.999$, $\bar{Z}=2.16$;
at 8–12 MPa, $u=11.24p^{-0.065}$, $r=0.938$, $\bar{Z}=1.05$;
at 14–22 MPa, $u=1.19p^{0.813}$, $r=0.999$, $\bar{Z}=1.14$;

For CMDB100:

at 2–8 MPa, $u=6.96p^{0.230}$, $r=0.973$, $\bar{Z}=1.75$;

Fig.6 Burning rate curves of DB001

Fig.7 Burning rate curves of CMDB100

Fig.8 Relationship of catalytic efficiency and text pressure at 2–8 MPa in DB001

Fig.9 Relationship of catalytic efficiency and text pressure at 2–8 MPa in CMDB100

at 4–12 MPa, $u=7.71p^{0.176}$, $r=0.978$, $\bar{Z}=1.24$;

at 14–20 MPa, $u=1.26p^{0.902}$, $r=0.999$, $\bar{Z}=0.88$.

Fig.8 shows that the value of Z is higher than 2 at 2–8 MPa, and that the pressure exponent of DB100 propellant is reduced by 64% from 0.805 to 0.289 at 2–8 MPa. It is reduced to -0.065 at 8–12 MPa, which is in the range of “mesa effect”. From Fig.9, it can be seen that the value of Z is higher than 1.7 and the pressure exponent of CMDB propellant is reduced to 0.178 at 2–8 MPa, within the range of which “plateau combustion” occurs.

As one can see, LCBTATz as an auxiliary ballistic energetic modifier can be effective to increase the burning rate and reduce the pressure exponent of propellants. Especially, super burning effect occurs at low pressure and the “mesa effect” occurs at 8–12 MPa in the DB propellant. The pressure exponent of CMDB100 is reduced to 0.178, and “plateau combustion” occurs at 4–12 MPa.

4 Conclusions

The lead complex based BTATz(LCBTATz) was prepared, characterized, and investigated. It was used as a catalyst for DB001 and CMDB100. The reaction kinetic equations of the main exothermal decomposition processes of DB001 and CMDB100 are $da/dt = 10^{16.91} \times (\alpha^{-1}/2) \times \exp(-1.76 \times 10^5/RT)$ and $da/dt = 10^{17.77} \times 2(1-\alpha)^{3/2} \times \exp(-1.78 \times 10^5/RT)$, respectively. The results of evaluating the thermal safety for the propellants

were obtained as: (1) for DB001, $T_{SADT}=444.50$ K, $T_{TIT}=453.96$ K, $T_b=471.84$ K; when $E_K=182500$ J·mol⁻¹, and $A_K=10^{18.20}$ s⁻¹, $t_{Tlad}=39.36$ s, $\Delta S=99.87$ J·mol⁻¹·K⁻¹, $\Delta H=178.66$ kJ·mol⁻¹, $\Delta G=132.56$ kJ·mol⁻¹; (2) For CMDB100, $T_{SADT}=442.38$ K, $T_{TIT}=452.89$ K, $T_b=464.13$ K; when $E_K=162100$ J·mol⁻¹, and $A_K=10^{15.9}$ s⁻¹, $t_{Tlad}=21.3$ s, $\Delta S=79.72$ J·mol⁻¹·K⁻¹, $\Delta H=169.36$ kJ·mol⁻¹, $\Delta G=133.18$ kJ·mol⁻¹. With the help of the ballistic modifier in the DB propellant formulation, the burning rate can be improved by 208.4% at 2 MPa and 126.5% at 4 MPa, and the pressure exponent can be reduced to -0.06 at 8–12 MPa. Also, in the CMDB propellant formulation, the burning rate can be improved by 159.2% at 2 MPa, the pressure exponent can be reduced to 0.18 at 4–12 MPa. The results show that LCBTATz has obvious catalysis in increasing the rate and excellent ability to reduce pressure index in the combustion of double-base propellants. Compared with other general lead compounds, or nanocompounds, LCBTATz can either enhance the burning rate or lower pressure index in DB propellants, which is a kind of high efficient combustion catalyst at the rang of medium and low pressure.^{33–38}

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