CuO/PbO Nanocomposite: Preparation and Catalysis for Ammonium Perchlorate Thermal Decomposition

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ABSTRACT: In this present article, we reported a facile and efficient milling method to prepare a series of CuO/PbO nanocomposite metal oxides (CuO/PbO NMOs), with CuO/PbO molar ratios of 1:2, 1:1, 1:0.5, and 1:0.25 as a potential catalyst to catalyze the thermal decomposition of ammonium perchlorate (AP). The obtained CuO/PbO NMOs were systematically characterized. X-ray diffraction (XRD), X-ray energy-dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS) analyses showed that the characteristic peaks of CuO/PbO NMOs were almost the superposition of nano CuO and nano PbO, while few new weak peaks were observed resulting from the lattice defects and new structural arrangements and chemical bonds between nano CuO and nano PbO during a high-energy grinding process. Scanning electron microscopy (SEM) and transition electron microscopy (TEM) observations exhibited that the particle sizes of the CuO/PbO NMOs were distributed in the range of 10−20 nm. Thermogravimetric (TG) analysis coupled with differential scanning calorimetric (DSC) techniques verified that CuO/PbO NMOs with a CuO/PbO molar ratio of 1:1 presented the best catalytic effect for AP thermal decomposition among the other CuO/PbO NMOs, as well as the single nano CuO and nano PbO. The outstanding catalytic performance is mainly reflected as follows: shifting the peak temperature of AP in high-temperature decomposition stages from 441.3 to 347.6 °C, increasing the decomposition heat of AP from 941 to 1711 J/g, and decreasing the Gibbs free energy of AP from 199.8 to 172.1 kJ/mol, supporting the existence of a synergistic catalytic effect between nano CuO and nano PbO.

1. INTRODUCTION

With the ongoing advances in nanotechnology, nanoscale transition-metal oxides have gained much attention in the field of catalyzing ammonium perchlorate (AP) and AP-based propellants in recent years. Nanocatalysts exhibit better catalytic effects than traditional catalysts, owing to their small particle size, large specific surface area, and an abundance of catalytic active sites. Nanoscale transition-metal oxides have received intense attention due to their good catalytic performance for AP and AP-based propellants. For example, Song et al. prepared α-Fe2O3 nanotubes and found that α-Fe2O3 nanotubes at 2 wt % displayed enhanced catalytic activity for the thermal decomposition of AP. Elbasuney and Yehia fabricated AP encapsulated with nano CuO and found that at 1 wt %, nano CuO demonstrated superior catalytic ability by decreasing the temperature of the endothermic decomposition stage by 30% and the two main exothermic decomposition peaks merged into a single peak with a 53% increase in the total heat release. Pang et al. introduced PbO nanoparticles into the AP/HTPB composite solid propellant. It was found that 1% content of the PbO nanoparticles boosted the burning rate of the propellant and lowered the pressure exponent. In addition, other nanoscale transition-metal oxides such as TiO2, NiO, and ZnO also showed effective catalytic ability for AP and AP-based propellants. Furthermore, it was shown that nanocomposite metal oxides had higher catalytic efficiency for AP and AP-based propellants than the single nanoscale metal oxides. Wang et al. found that the catalytic performance of the nano CuO/Fe2O3 composite metal oxides for AP thermal decomposition was much better than those of nano CuO and nano Fe2O3 because of synergistic catalytic effects. Compared to that of the basic composite propellant, the burning rate of the propellant with 1% nano CuO/Fe2O3 increased by approximately 55%, while the pressure index was almost unchanged. Hosseini et al. synthesized a series of hybrid CuO/NiO nanoparticles and...
found that the catalytic performance of CuO/NiO nanoparticles with a Cu/Ni molar ratio of 1:2 for AP thermal decomposition was significantly superior to those of CuO nanoparticles only and NiO nanoparticles only. This was ascribed to the synergistic catalytic effects of nano CuO and nano NiO for AP.\textsuperscript{17,18} They also synthesized CuO/Cr\textsubscript{2}O\textsubscript{3} spinel nanoparticles and found that in the presence of Cu–Cr–O nanocatalysts, all of the exothermic peaks of AP moved to lower temperatures, indicating enhanced thermal decomposition of AP. Moreover, the released heat of AP was increased to 1490 J/g in the presence of a Cu–Cr–O nanocatalyst. This phenomenon was attributed to the mixed valence of Cu\textsuperscript{2+} and Cr\textsuperscript{3+} ions in the Cu–Cr–O nanocatalyst.\textsuperscript{16} Inspired by these reports, we propose that a nanoscale CuO–PbO composite may be a good candidate material for obtaining improved nanoscale metal oxide catalysts for AP thermal decomposition. To the best of our knowledge, the preparation of CuO/PbO NMOs and their use for AP thermal decomposition catalysis have not been reported in the literature.

To date, many different methods have been used to prepare nanocomposite catalysts. Microemulsion and sol–gel syntheses are common methods for the preparation of nanocomposites, but they are not environmentally friendly due to the use of organic solvents.\textsuperscript{17,18} A coprecipitation method and a solid–phase reaction method have also been used to obtain nanocomposite catalysts; however, it is difficult to precisely control the size distribution of the obtained nanocatalysts using these methods.\textsuperscript{19,20} Furthermore, none of the methods mentioned above can be used for batch production and therefore are not suitable for large-scale application in the propellant industry. In our previous study, the CuO/Fe\textsubscript{3}O\textsubscript{4} nanocomposite metal oxide was effectively synthesized on a large scale by milling without using harmful solvents.\textsuperscript{21} Hence, the milling method is an ideal candidate strategy for the preparation of the CuO/PbO nanocomposite metal oxide (CuO/PbO NMO) catalysts.

In this study, CuO/PbO NMOs with various molar ratios were prepared on a large scale by milling method, and their catalytic properties for AP thermal decomposition were studied by thermal gravimetric analysis combined with differential scanning calorimetry (TG-DSC). It was found that the obtained CuO/PbO NMOs show good catalytic performance for AP thermal decomposition and therefore are promising candidate materials for further application in AP and AP-based propellants.

2. MATERIALS AND METHODS

2.1. Materials. All chemicals were analytical grade reagents except AP and were used as received without further purification. CuO and PbO were purchased from Sinopharm Chemical Reagent Co., Ltd. C\textsubscript{2}H\textsubscript{5}OH was purchased from Nanjing Chemical Reagent Co., Ltd. N-CuO with an average diameter of 10–20 nm and N-PbO with an average diameter of 20–30 nm were prepared by milling. AP with an average diameter of 64 μm was of industrial grade and was purchased from Dalian North Potassium Chlorate Co., Ltd.

2.2. Preparation of CuO/PbO NMOs. CuO/PbO NMOs were prepared by milling. The raw materials CuO and PbO were mixed at different molar ratios (1:2, 1:1, 1:0.5, and 1:0.25) to form a 1 kg mixture. A 9–12 kg alcohol–water dispersion was prepared, in which the ratio of ethanol to deionized water was 1:1. A certain proportion of the mixture was added to the dispersion and the mass concentration of the mixture in the slurry was kept strictly at 8–10%. The slurry was ground and crushed in an HLG-5 nanometer pulverizer. The speed of rotation was in the range of 1200–1300 rpm. The outlet temperature of the slurry was controlled in the range of 20–30 °C by an industrial AC-20 chiller. After grinding for 2–3 h, a CuO/PbO NMO slurry was obtained. The supernatant of the slurry was removed by siphoning after the slurry settled naturally. Then, the slurry was thoroughly stirred and transmitted to dry in a vacuum freeze dryer. Finally, CuO/PbO NMOs having good dispersibility were obtained. The preparation processes of N-CuO and N-PbO were similar.

2.3. Preparation of a CuO/PbO NMO/AP Mixture. A CuO/PbO NMO/AP mixture was obtained by light grinding. Here, the purpose of light grinding was mainly to minimize the change in the particle size of AP during the grinding process. At a mass ratio of 49:1, the AP and CuO/PbO NMOs were mixed and added to an appropriate amount of ethyl acetate. Then, the mixture sample was lightly ground. After the evaporation of the solvent and complete drying of the mixture sample, the CuO/PbO NMO/AP mixture was obtained. The thermal decomposition of CuO/PbO NMO/AP was characterized by TG-DSC thermal analysis. The catalytic properties of CuO/PbO NMOs were characterized by the thermal decomposition peak and apparent decomposition heat of the AP mixture. The catalytic properties of AP with N-CuO, N-PbO, and N-CuO/PbO (mix) were also studied.

2.4. Measurements and Characterizations. The morphological characterizations of the as-prepared samples were performed on an S-4800II field scanning electron microscope (SEM). The powder X-ray diffraction (XRD)
patterns of the samples were recorded on a Bruker D8 Advance X-ray diffractometer equipped with a Cu Kα source. Energy-dispersive spectroscopy (EDS) images were recorded by a Hitachi SU8000 to characterize the morphologies and element distribution of the samples. X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI QUANTERA II X-ray photoelectron spectrometer to estimate the valence state of the elements. Transmission electron microscopy (TEM) was performed on a Tecnai 12 microscope (FEI Corporation).

The catalytic effect of the as-synthesized CuO/PbO NMOs on the thermal decomposition of AP has been demonstrated by a differential scanning calorimetry, thermogravimetry, and differential thermogravimetry (DSC-TG-DTG) method using an SDT Q600 synchronous thermal analyzer. The tested samples were heated from 50 to 500 °C at a heating rate of 20 °C/min under a N2 flow rate of 20 mL/min.

2.5. Catalytic Property. Thermogravimetric (TG) analysis and differential scanning calorimetric (DSC) techniques were used to investigate the thermal decomposition of a mixture of CuO/PbO NMO/AP using an SDT Q600 thermal analyzer at 20 °C/min from 50 to 500 °C with a nitrogen flow rate of 20 mL/min. Pure AP and AP mixtures with N-CuO and N-PbO were also measured for comparison. In addition, at different heating rates of 5, 10, 15, and 20 °C/min, the kinetic data were calculated from the corresponding DSC data of the AP samples.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis. The XRD patterns of single metal oxides of nano CuO, nano PbO, nano PbO/CuO mixture, and CuO/PbO NMOs are presented in Figure 1. CuO/PbO NMOs with CuO/PbO molar ratios of 1:2, 1:1, 1:0.5, and 1:0.25 were denoted as N-CuO/PbO(1:2), N-CuO/PbO(1:1), N-CuO/PbO(1:0.5), and N-CuO/PbO(1:0.25), respectively. For single metal oxides of nano CuO and nano PbO, all major diffraction peaks could be perfectly assigned to monoclinic CuO (PDF no. 65-2309) and tetragonal PbO (PDF no. 65-0399), respectively.

3.2. Surface Elemental Composition and Atom Content for CuO/PbO NMOs

| samples             | Cu/% | Pb/% | O/%  | n(CuO)/n(PbO) |
|---------------------|------|------|------|---------------|
| N-CuO/PbO(1:2)      | 17.74| 34.68| 45.05| 1:1.955       |
| N-CuO/PbO(1:1)      | 19.72| 20.03| 55.58| 1:1.016       |
| N-CuO/PbO(1:0.5)    | 29.05| 14.55| 53.33| 1:0.501       |
| N-CuO/PbO(1:0.25)   | 42.90| 10.58| 43.34| 1:0.247       |

Figure 2. EDS spectra of CuO/PbO NMOs.

Figure 3. EDS elemental mappings of N-CuO/PbO(1:1): (a) SEM, (b) O/Cu/Pb element, (c) O element, (d) Cu element, and (e) Pb element.
those of nano CuO and nano PbO, and the result showed that there was no interaction in the nano CuO/PbO mixture.

In the XRD patterns of CuO/PbO NMOs, with an increase in the CuO/PbO molar ratio, the peak intensities of the (002) and (111) crystal planes of nano CuO increased gradually, while the peak intensity of the (101) crystal plane of nano PbO decreased gradually. Moreover, there was a partial overlap between the peak of the (002) crystal plane of nano CuO and the peak of the (010) crystal plane of nano PbO. The XRD diffraction peaks of CuO/PbO NMOs were almost the superposition of the diffraction peaks of single metal oxides of nano CuO and nano PbO, while few new weak peaks were observed in the 22°–24° range. Simultaneously, the XRD diffraction peak intensities of CuO/PbO NMOs were generally low. The few new weak peaks and weak peak intensities may be explained as follows: (1) Under the high-speed grinding force, the atoms of CuO and PbO are intermingled so that new bonds are created between the atoms, giving rise to a variety of different structural arrangements incorporating both Cu and Pb and a broad XRD signal. Therefore, some chemical interactions between CuO and PbO or Cu and Pb may be present in CuO/PbO NMOs. (2) Because of the effect of the high-speed grinding force, the crystal lattices of single metal oxides of nano CuO and nano PbO were distorted during the fabrication of CuO/PbO NMOs, resulting in the appearance of lattice defects and generation of a more disordered crystal structure. A larger number of amorphous crystal structures weaken the diffraction peak intensity of CuO/PbO NMOs and give rise to miscellaneous peaks.

The particle sizes of CuO/PbO NMOs can be predicted by the Scherrer equation (eq 1). It presents the relationship between diffraction angles (2θ: 28.6 and 35.8°) and half-peak widths (B: 0.474 and 0.466°) of the characteristic diffraction peak in the XRD pattern. 

\[ D = \frac{0.89\lambda}{B \cos \theta} \]  

where D is the estimated particle size, \( \lambda \) is the wavelength of the incident X-ray beam, B is the half-peak width of the diffraction peak, and \( \theta \) is the diffraction angle. For N-CuO/PbO(1:1) that shows the best catalytic properties (see below), using the Scherrer equation, the particle sizes of CuO/PbO NMOs were calculated to be 17.1 and 17.7 nm, respectively.

### 3.2. EDS Analysis

EDS analysis was carried out to detect the surface elemental composition of CuO/PbO NMOs, and the results are shown in Figure 2.

A comparison of Figure 2 shows that CuO/PbO NMOs were mainly composed of Cu, Pb, and O elements. The signals of Au and Al elements, in the EDS spectra, originate from electric gilding and sample pedestal, respectively. The surface elemental composition and atom content for CuO/PbO NMOs are presented in Table 1.

As observed from the data presented in Table 1, CuO/PbO molar ratios in CuO/PbO NMOs were essentially identical to the corresponding feeding ratios. The observed slight differences between the feeding ratios and composite molar ratios were most likely due to the errors in purity, weight, and the testing process. These results indicated that nano CuO and nano PbO in CuO/PbO NMOs were evenly distributed on the microscopic scale.

To further explore the uniformity of CuO/PbO NMOs, EDS elemental mapping was performed for N-CuO/PbO(1:1) as the representative sample, and the results are shown in Figure 3.

It is obvious from Figure 3 that the elements of Cu and Pb in N-CuO/PbO(1:1) were distributed uniformly even in a small area with the dimensions of 20 μm × 15 μm, confirming the uniform distributions of nano CuO and nano PbO in the CuO/PbO NMOs prepared through the milling approach.
The surface chemical composition of N-CuO/PbO(1:1) was investigated by XPS analysis. Figure S1a−c displays the XPS spectra of single metal oxides of nano CuO and nano PbO and N-CuO/PbO(1:1), respectively.

As shown in Figure S1a, the peaks located at 933.0 and 952.8 eV were assigned to the Cu 2p3/2 and Cu 2p1/2 of the oxidized Cu(II) species, respectively. Additionally, two satellite peaks (marked as sat.) at approximately 942.3 and...
962.0 eV verify the existence of pure CuO. The peak in the O 1s spectrum at approximately 529.7 eV can be indexed as the oxygen of CuO. The other peak with a higher binding energy of 531.2 eV is mainly attributed to the chemisorbed hydroxyl oxygen. Figure 2b shows the XPS spectra of nano PbO, and the peaks at 138.4 and 143.3 eV, respectively, can be assigned to the Pb 4f7/2 and Pb 4f5/2 states of Pb2+, while the O 1s spectrum presents a peak at 531.3 eV, approximately close to that at 530.9 eV for O 1s in PbO from the literature.30 The XPS spectra of N-CuO/PbO(1:1) were similar to those of nano CuO and nano PbO. However, the peak in the O 1s spectrum at 529.7 eV of CuO almost disappeared and the peaks of Pb and Pb−O shifted down from their initial position. These showed that the structures of CuO and PbO changed in N-CuO/PbO(1:1) due to defect formation and possible changes in the chemical bonding, which is consistent with the XRD results. The XPS peak positions of the different samples and their assignments are described in Table 2.

### 3.3. Micromorphology

The SEM images of nano CuO, nano PbO, and different CuO/PbO NMOs are shown in Figure 4. We found that the diameter ranges of nano CuO and nano PbO were 10−20 and 20−30 nm, respectively. The particles of different CuO/PbO NMOs were small in size with diameters in the range of 10−20 nm.

TEM images of nano PbO and N-CuO/PbO(1:1) are shown in Figure 5. The particle size for both nano PbO and N-CuO/PbO(1:1) was in the 10−20 nm range, which is in agreement with their SEM and XRD results.

### 3.4. Thermal Analysis

#### 3.4.1. Effect of the Molar Ratio of N-CuO/PbO on the Catalytic Performance

To study the catalytic properties of different N-CuO/PbO, the thermal decomposition of AP and AP composites with different molar ratios of N-CuO/PbO is shown in Figure 7. The thermal decomposition parameters are listed in Table 3. The thermal analysis results showed that the catalytic performance of different CuO/PbO NMOs was improved with increasing molar ratio of PbO.

| samples                      | $T_l/°C$ | $T_h/°C$ | $T_e/°C$ | $T_{mc}/°C$ | $Q/(J/g)$ | $R/%$ |
|------------------------------|---------|---------|---------|------------|----------|------|
| 64 μm AP [21]               | 322.3   | 441.3   | 307.1   | 440.1      | 436.0    | 941  |
| 2% N-CuO/PbO(1:2)/AP        | 333.6   | 373.5   | 305.8   | 375.2      | 370.2    | 1689 |
| 2% N-CuO/PbO(1:1)/AP        | 314.0   | 347.6   | 289.4   | 351.5      | 345.1    | 1711 |
| 2% N-CuO/PbO(1:0.5)/AP      | 329.3   | 372.7   | 302.7   | 373.2      | 370.7    | 1706 |
| 2% N-CuO/PbO(1:0.25)/AP     | 320.6   | 368.5   | 296.4   | 369.2      | 366.7    | 1725 |
| 2% nano CuO/AP [21]         | 322.3   | 358.3   | 295.5   | 362.3      | 350.5    | 1821 |
| 2% nano PbO/AP              | 325.4   | 400.9   | 302.6   | 401.0      | 397.3    | 1587 |
| 2% N-CuO/PbO(1:1(mix))/AP   | 329.2   | 372.4   | 305.3   | 372.8      | 370.1    | 1619 |

Note: $T_l$ and $T_h$, peak temperatures of the mass loss rate in the low-temperature and high-temperature decomposition stages, respectively; $T_e$, the initial decomposition peak temperature; $T_{mc}$, the termination decomposition peak temperature; $T_{mc}$, the maximum weight loss temperature, $Q$, decomposition heat; and R, the growth rate of Q of the catalytic system relative to that of pure AP.
catalysts was evaluated by TG-DSC. The relative curves and thermal decomposition parameters are shown in Figure 6 and Table 3. The curves of pure AP (Figure 6a) exhibited three-stage decomposition:21,31,32 the crystal transition endothermal stage in the 240–250 °C range, the low-temperature pyrolysis stage (LTP) in the 300–330 °C range, and the high-temperature pyrolysis stage (HTP) 400–480 °C range. As shown in the TG curve, all of the systems exhibited two weight loss steps, corresponding to LTP and HTP of AP pyrolysis processes, respectively. When CuO/PbO NMOs were added to reach a weight fraction of 2%, its $T_h$ was reduced compared to that for pure AP, and its HTP and LTP peaks merged into a single peak, so only one weight loss step was present in the TG curve. The $T_h$ values of samples b–e decreased compared to that of the pure AP, and the AP HTP peak temperatures decreased from 441.3 to 373.5, 347.6, 372.7, and 368.5 °C (decreasing by 67.8, 93.7, 68.6, and 72.8 °C), respectively. In addition, the apparent decomposition heat of AP increased from 941 to 1556, 1711, and 1758 J/g, respectively, and $T_a$ increased by 10.7, 53.3, and 24.8 °C, respectively. Compared to the three mixtures of samples f–h, the $T_h$ of sample b increased by 10.7, 53.3, and 24.8 °C, respectively, and it also had a high decomposition heat. These results indicated that the catalytic effect of CuO/PbO NMOs was better than those of the single nanocatalysts and the mixed catalyst.

The excellent catalytic performance of N-CuO/PbO on AP was attributed to the p-type semiconductors of CuO and PbO.33 Comparison of single nano CuO, single nano PbO, and N-CuO/PbO(1:1) showed that under the action of high-energy milling force, nano CuO and nano PbO in N-CuO/PbO fully realize electron–hole recombination on the mesoscopic scale due to the greater amount of lattice defects and holes, which can further accelerate the electron transfer in AP thermal decomposition.

Figure 7 presents the DSC curves of different catalytic systems for AP pyrolysis at different heating rates. The kinetic parameters for the exothermic decomposition of AP and AP composites with different nanocatalysts were obtained by the Kissinger method.34 Kissinger’s equation can be expressed as eq 2.

\[ \ln \left( \frac{\beta}{T_p^2} \right) = - \frac{E_a}{R T_p} + \ln \left( \frac{A R}{E_a} \right) \]  

where $\beta$ is the heating rate (°C/min), $T_p$ is the peak temperature of the HTP, $R$ is the gas constant (8.314 J/(mol·K)), $E_a$ is the activation energy (J/mol), and $A$ is the pre-exponential factor.

The kinetics parameters of thermal decomposition of different AP samples can be gained by plotting $\ln(\beta/T_p^2)$ versus $1000/T_p$ (Figure 8), and the results are listed in Table 4.

The rate constant ($K$), activation enthalpy ($\Delta H^r$), activation entropy ($\Delta S^r$), and activation Gibbs free energy ($\Delta G^r$) of the

Table 5. Thermodynamics/Kinetic Parameters for Pyrolysis of Different AP Samples

| samples             | $E_a$ (kJ/mol) | $\ln A$ (s$^{-1}$) | $K$ ($T_p$) (s$^{-1}$) | $\Delta S^r$ (J/(mol·K)) | $\Delta H^r$ (kJ/mol) | $\Delta G^r$ (kJ/mol) |
|---------------------|----------------|---------------------|------------------------|--------------------------|-----------------------|-----------------------|
| 64 μm AP [21]       | 156.7          | 22.1                | 2.66 × 10$^{-3}$       | −68.6                    | 150.8                 | 199.8                 |
| 2% nano CuO/AP [21] | 113.4          | 17.1                | 1.14 × 10$^{-2}$       | −108.8                   | 108.2                 | 176.8                 |
| 2% N-CuO/PbO(1:1)   | 102.3          | 14.4                | 9.58 × 10$^{-3}$       | −131.4                   | 97.0                  | 181.8                 |
| 2% N-CuO/PbO(1:1)   | 178.8          | 30.6                | 1.76 × 10$^{-2}$       | 3.4                      | 173.6                 | 171.5                 |
| CuO/AP              | 120.1          | 21.8                | 5.99 × 10$^{-3}$       |                          |                       |                       |

Figure 8. Dependence of $\ln(\beta/T_p^2)$ ∼ 1000/$T_p$ for high-temperature decomposition of AP samples: (a) pure AP, (b) AP with 2% nano CuO, (c) AP with 2% N-CuO/PbO(1:1 mixes), and (d) AP with 2% N-CuO/PbO(1:2).

Table 6. Decomposition Heat of Different AP Systems

| content  | 0% | 1% | 2% | 3% | 4% |
|----------|----|----|----|----|----|
| Q (J/g)  | 941| 1556 | 1711| 1758| 1744|

Compared to the three mixtures of samples f–h, the $T_h$ of sample b increased by 10.7, 53.3, and 24.8 °C, respectively, and it also had a high decomposition heat. These results indicated that the catalytic effect of CuO/PbO NMOs was better than those of the single nanocatalysts and the mixed catalyst.

The excellent catalytic performance of N-CuO/PbO on AP was attributed to the p-type semiconductors of CuO and PbO.33 Comparison of single nano CuO, single nano PbO, and N-CuO/PbO(1:1) showed that under the action of high-energy milling force, nano CuO and nano PbO in N-CuO/PbO fully realize electron–hole recombination on the mesoscopic scale due to the greater amount of lattice defects and holes, which can further accelerate the electron transfer in AP thermal decomposition.

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where $\beta$ is the heating rate (°C/min), $T_p$ is the peak temperature of the HTP, $R$ is the gas constant (8.314 J/(mol·K)), $E_a$ is the activation energy (J/mol), and $A$ is the pre-exponential factor.

The kinetics parameters of thermal decomposition of different AP samples can be gained by plotting $\ln(\beta/T_p^2)$ versus $1000/T_p$ (Figure 8), and the results are listed in Table 4.

The rate constant ($K$), activation enthalpy ($\Delta H^r$), activation entropy ($\Delta S^r$), and activation Gibbs free energy ($\Delta G^r$) of the...
decomposition reaction of different AP samples were obtained using eqs 3–6, and the results are listed in Table S.

\[
K = A \exp \left( -\frac{E_a}{RT_p} \right)
\]

(3)

\[
\Delta H^\# = E_a - RT_p
\]

(4)

\[
\Delta S^\# = R[\ln A - \ln(K\beta T_p/h)]
\]

(5)

\[
\Delta G^\# = \Delta H^\# - T_p\Delta S^\#
\]

(6)

where \(K\) and \(h\) are the Boltzmann constant \((1.381 \times 10^{-23})\) and Planck’s constant \((6.626 \times 10^{-34})\), respectively.5

An examination of the data presented in Table S shows that with the addition of 2% nano CuO, N-CuO/PbO(1:1(mix)), and N-CuO/PbO(1:1), \(E_a\) and \(\Delta G^\#\) of AP were significantly reduced. The minimum \(\Delta G^\#\) and the maximum \(K\) were obtained for 2% N-CuO/PbO(1:1)/AP. \(K\) is a universal parameter to assess the reaction. The \(K\) value of 2% N-CuO/PbO(1:1)/AP was about 7 times that of 64 μm AP. This increase in \(K\) can be attributed to the easy facilitation of the decomposition reaction.37 These results indicated that the different catalysts studied in this work promoted the thermal decomposition of AP, with N-CuO/PbO(1:1) showing the best catalytic effect.

3.4.2. Effect of the Content on the Catalytic Performance.

Figure 9 shows the DSC curves of the thermal decomposition of different catalyst contents, and the decomposition heats are listed in Table 6.

With the increase of the content of N-CuO/PbO(1:1), the HTP peak of AP gradually shifted to lower temperatures. The addition of 1, 2, 3, and 4% contents of N-CuO/PbO(1:1) led to the shift of the HTP peak from 441.3 °C (pure AP) to 362.1, 347.6, 328.1, and 327.7 °C, respectively. As shown in Table 6, with the increase of the content of N-CuO/PbO(1:1), the decomposition heat of the AP samples first increased and then decreased, reaching a maximum value for the N-CuO/PbO(1:1) content of 3%. This trend can be explained as follows. The thermal decomposition reaction of AP is favored by the greater content of the catalyst active site and the greater content of AP. With increased N-CuO/PbO(1:1) content, the perchlorate acid released from decomposition of AP could react with the metal oxide, which then would change the heat releases, and there might be some other chemical reactions, whereas when the catalyst content exceeded 3%, the decomposition heat of N-CuO/PbO(1:1)/AP decreased due to the decreased content of AP in the mixture.

Generally, it is expected that a small content of the catalyst will be used to increase the decomposition heat of AP while reducing its HTP temperature. Therefore, it could be concluded that the addition of 3% N-CuO/PbO(1:1) to AP not only reduced the HTP temperature of AP but also increased its decomposition heat. This confirms that the N-CuO/PbO(1:1) added at a 3% content level presents excellent catalytic performance on AP decomposition.

4. CONCLUSIONS

(1) CuO/PbO NMO catalysts were prepared by the milling method for different compositions and it was found that their particle size was distributed in the 10–20 nm range. N-CuO/PbO with a CuO/PbO molar ratio of 1:1 showed the best catalytic effect on AP.

(2) Comparison of single nano CuO, single nano PbO, and N-CuO/PbO(1:1(mix)) catalysts showed that N-CuO/PbO(1:1) showed a synergistic catalytic effect. This effect may be attributed to the lattice distortion of nano PbO and nano CuO during high-energy grinding that resulted in lattice defects and new structural arrangements and chemical bonds. These features enhanced the catalytic activity of N-CuO/PbO(1:1). In conclusion, this study provides guidance for the preparation of improved nanocomposite metal oxide catalysts and their application in solid propellants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05050.

Additional experimental XPS results used in this study (PDF)

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Notes

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