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# New roles of metal–organic frameworks: Fuels for aluminum-free energetic thermites with low ignition temperatures, high peak pressures and high activity

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ABSTRACT

Aluminum-based thermites are widely used in gas generators, propulsions, explosives, and welding because these materials can release a large amount of stored energy on combustion. However, one of the biggest problems in the traditional aluminum-based thermite systems is excessive oxidation of the aluminum particle before combustion, resulting in a decrease of the active aluminum content. Here, we report a new-concept aluminum-free thermites based on an energetic metal–organic framework $[Cu(atrz)_3(NO_3)_2]_n$ (MOF(Cu), atrz = 4,4′-azo-1,2,4-triazole) as a fuel. Compared with the traditional aluminum-based thermites, these new thermites exhibit superior performances such as low electrostatic discharge sensitivities, low ignition temperatures, high heats of reaction, high peak pressures, high activity, and production of very few solid residues. It is anticipated that this work will open a new field for the application of MOFs, while laying the groundwork for the development of new energetic materials.


## 1. Introduction

Because of its high reaction enthalpy and good thermal conductivity, aluminum (Al) powders at the micrometer size range are broadly employed as fuels in conventional thermites, which are regularly used in gas generators, propulsions, explosives, thermal batteries, weldings, material synthesis, and waste disposals [1–3]. Although these thermites usually have higher energy density than organic explosives such as 2,4,6-trinitrotoluene (TNT), nitrocellulose, cyclotrimethylenetrinitramine (RDX), etc., they suffer from slow rates of energy release and super-high ignition temperatures (~2000 °C) [4,5]. In practical applications, a large portion of the aluminum powders often remain unreacted due to low reaction rates and long ignition delays; as a result, the energetic properties are limited [4,6]. Alternatively, nanothermites, a subset of metastable intermolecular composites (MIC), are a relatively new class of energetic materials comprising a metallic fuel and an oxidizer at nanoscale that can rapidly release heat and pressure. In most formulations, nanoaluminum is employed as fuel because of its superior properties, and ready availability of an oxidizer (e.g., CuO, $Fe_2O_3$, $MoO_3$, etc.) [7–12]. Unfortunately, current aluminum-based nanothermites still suffer from high electrostatic sensitivities [13,14], and relatively high ignition temperatures (~800 °C) [13,15,16]. Meanwhile, the higher surface energy of the nanoparticles also leads to greater particle aggregation, and increases composite agglomeration, which could lead to the composite incomplete combustion [17,18]. Apart from these, however, one of the biggest problems in the aluminum-based thermite systems is excessive oxidation of the aluminum particle before combustion, resulting in a decrease of the active aluminum content. Moreover, most of the aluminum-based thermites have relatively low peak pressures (maximum peak pressure) mainly due to the lack of gas elements (e.g., CHON elements) in their components, which lead to few gaseous products during combustion. Nevertheless, gas generation plays an important role in the altitude control of orbiting microspacecraft and in microscale devices capable of producing tens of milliNewtons (mN) of thrust [19,20]. Hence, developing new thermites with low ignition temperatures, high peak pressures, and high activity would be very fascinating while challenging at the same time.

As an emerging class of porous materials, metal–organic frameworks (MOFs) have recently attracted considerable attention due to their high surface area, uniform pore size, controllable structures, and readily tailorable functions [21–28]. Energetic MOFs are

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an appealing subclass and can be mainly constructed from energetic nitrogen-rich ligands and metal ions [29–31]. Compared with aluminum powders, energetic MOFs possess good stabilities, abundant gas elements (e.g., high nitrogen contents) and high heats of detonation, which would make them as ideal alternative fuels to develop a new-concept aluminum-free thermite and solve above problems. Recently, we had reported MOFs as an active component for green gas generators [32]. However, there has so far been no report about the exploration of MOFs in thermite systems, although a lot of energetic MOFs with fascinating topological structures have been synthesized over the past few years [33–35].

Here, we reported a novel type of thermites based on a three-dimensional (3D) energetic MOF $[Cu(atrz)_3(NO_3)_2]_n$ [MOF(Cu), atrz = 4,4′-azo-1,2,4-triazole]. The energetic performances of these materials in terms of ignition temperature, heat of reaction, peak pressure, reactivity and sensitivity were assessed and compared to existing and more traditional aluminum-based thermites, exhibiting impressive energetic properties. We chose to use MOF(Cu) as the fuel for the following reasons: (1) MOF(Cu) possesses a super-high heat of detonation and a high nitrogen content (53.35%) [33], which could improve the energetic performances of the target thermites; (2) in comparison with aluminum powders, MOF(Cu) exhibits higher activity since its decomposition temperature is 243 °C, which could contribute to decreasing the ignition temperatures of the target thermites. In addition, the perchlorate salts were selected as the oxidizers because of their high oxygen contents and strong oxidizing nature, which have inspired many fascinating studies [15,36,37].

## 2. Experimental section

### 2.1. Caution

Although we have not experienced any problems during the preparation of thermites, standard safety precautions (leather gloves, face shield and ear plugs) should be taken when handling these materials.

### 2.2. Chemical and materials

$NH_4ClO_4$ and $KClO_4$ were all purchased from Beijing Chemical Reagent Company without further purification. 50 nm copper oxide (CuO) was purchased from Sigma-Aldrich Corporation. 50 nm aluminum (Al) nanopowders were purchased from Beijing DK Nano Technology Co. LTD, and the purity of the aluminum nanoparticle was 80%, from the manufacturer's data, which have further been confirmed by thermogravimetric/differential scanning calorimetry measurement (TG/DSC, Fig. S15).

### 2.3. Instrumentation

Powder X-ray diffraction (PXRD) patterns of the samples were analyzed with monochromatized Cu-K$\alpha$ ($\lambda = 1.54178$ Å) incident radiation by Bruker D8 Advance X-ray diffractometer operating at 40 kV voltage and 50 mA current. PXRD patterns were recorded from 5° to 80° ($2\theta$) at 298 K. Infrared (IR) spectrum was recorded on a Bruker Tensor 27 spectro-photometer with HTS-XT (KBr pellets). X-ray photoelectron (XPS) spectrum was recorded on an AXIS Ultra X-ray photoelectron spectroscopy (Kratos Corporation, England). Elemental analysis was performed on an Elementar Vario EL (Germany). Field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was used to characterize the morphology (5 kV accelerating voltage, gold coating) and element analysis (at 20 kV accelerating voltage) of the thermites. PY/P&T-GC/MS (EGA/PY-3030D instrument, Frontier Lab, Japan; GC/MS, QP2010-Ultra) was used to characterize the gaseous combustion products of MOF(Cu)/$NH_4ClO_4$, 1 mg of sample was used and the temperature was programmed to 300 °C with the rate of 10°C $min^{-1}$ in 1.0 mL $min^{-1}$ He gas flow.

### 2.4. Preparation of MOF(Cu)

According to the literature procedure [33], atrz (1.5 mmol, 0.246 g) in 40 mL of boiling $H_2O$ was added into a 20 mL $Cu(NO_3)_2$•$3H_2O$ (0.45 mmol, 0.109 g) boiling aqueous solution. The mixed solution was stirred for 1 h, and then the resulting solution was filtered. Blue crystals were obtained by slow evaporation in a glass vial within several days. Yield: 81%. PXRD (Fig. S4), IR (Fig. S5), and elemental analysis confirmed that the structure of as-prepared sample is consistent with that of the reported MOF(Cu).

### 2.5. Preparation of the energetic thermites

$NH_4ClO_4$, $KClO_4$ were stoichiometrically mixed with MOF(Cu), respectively. Approximately, 10 mL of hexane was then added and the mixtures were ultrasonicated for 30 min to ensure intimate mixing. The hexane was allowed to evaporate in air and then the samples were placed in vacuum at 60 °C for 12 h to remove any remaining hexane and moisture. The powder was very gently broken with a spatula until the consistency for each sample was that of a loose powder. According to the stoichiometric calculation, MOF(Cu)/$NH_4ClO_4$ thermite contains 36.3% MOF(Cu) and 63.7% $NH_4ClO_4$, and MOF(Cu)/$KClO_4$ thermite contains 43.6% MOF(Cu) and 56.4% $KClO_4$.

The synthetic procedures of aluminum-based thermites are consistent with those of MOF(Cu)-based thermites. Al/$NH_4ClO_4$ thermite contains 32.4% Al and 67.6% $NH_4ClO_4$. Al/$KClO_4$ thermite contains 39.4% Al and 60.4% $KClO_4$. Al/CuO thermite contains 22% Al and 78% CuO.

The synthetic procedure of energetic composites (atrz/$Cu(NO_3)_2$/$NH_4ClO_4$ and atrz/$Cu(NO_3)_2$/$KClO_4$, reference samples) are consistent with those of MOF(Cu)-based thermites, and their stoichiometric ratios are also consistent with those of their corresponding MOF-based thermites. Atrz/$Cu(NO_3)_2$/$NH_4ClO_4$ contains 26.2% atrz, and 10.1% $Cu(NO_3)_2$ and 63.7% $NH_4ClO_4$. Atrz/$Cu(NO_3)_2$/$KClO_4$ contains 31.6% atrz, and 12.0% $Cu(NO_3)_2$ and 56.4% $KClO_4$.

### 2.6. Measurement of heat of reaction and ignition temperature using DSC/TG

In our study, a TA-DSC Q2000 differential scanning calorimeter was employed to determine the ignition temperatures, heats of reaction and compatibility of thermites. About 1.5 mg of sample was used and the temperature was programmed to 1000 °C (1273 K) at the rate of 10 °C $min^{-1}$ in 60 mL $min^{-1}$ $N_2$ flow. A minimum of three measurements were taken for each composite under identical experimental conditions to quantify the error. The ignition temperature was usually regarded as the onset temperature of an exothermic reaction and also as the lowest temperature that can induce the thermal explosion of a sample. The heat of reaction was obtained by the integration of the exothermic peaks.

### 2.7. Measurement of impact sensitivity

The impact sensitivity was tested on a type 12 tooling according to "up and down" method (Bruceton method). A 2.5 kg weight was dropped from a set height onto a 20 mg sample placed on 150 grit garnet sandpaper. Each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened. 50 drops were made from different heights, and an explosion or non-explosion was recorded