Effects of oxidizer structure on thermal and combustion behavior of Fe$_2$O$_3$/Zr thermite

Chunhong Li$^{1,2}$ and Xiaoli Kang$^3$

$^1$ School of Materials Science and Engineering, Xihua University, Chengdu 610039, People’s Republic of China
$^2$ Civil-Military Integration Key Laboratory for Advanced Energetic Materials and Devices, Xihua University, Chengdu 610039, People’s Republic of China
$^3$ E-mail: kangxiaoli515@126.com

Keywords: MOF-derived Fe$_2$O$_3$, oxidizer, thermite, combustion characteristics

Supplementary material for this article is available online

Abstract

Performance of MOF-derived micrometer porous Fe$_2$O$_3$ as the oxidizer in Zr-fuelled thermite is compared with commercial nano-sized Fe$_2$O$_3$ by characterizing thermal and combustion behavior of Fe$_2$O$_3$/Zr mixture via differential scanning calorimetry, optical emission measurement as well as composition and morphology analysis on condensed combustion products. Results show that thermal behaviors of Fe$_2$O$_3$/Zr with a slow heating rate have little difference regardless of the kind of Fe$_2$O$_3$. However, MOF-derived micrometer porous Fe$_2$O$_3$ show an obvious superiority in enhancing combustion of Fe$_2$O$_3$/Zr heated by a high rate. Combustion reactions of Fe$_2$O$_3$/Zr under high heating rates are probably rate-controlled by condensed reaction. The better performance of MOF-derived Fe$_2$O$_3$ is attributed to its larger contact area with Zr particle in that micrometer porous Fe$_2$O$_3$ particles are easily broken into primitive nano-sized particles, which effectively avoid the agglomeration of oxidizer. The MOF-derived Fe$_2$O$_3$ particles obtained at calcination temperature of 550 °C enable the best combustion performance of Fe$_2$O$_3$/Zr thermite. This should be because the crystallinity and porous structure of 550 °C-Fe$_2$O$_3$ are more favorable for the mass transfer process during high-rate combustion.

1. Introduction

Zirconium (Zr) has good ignitibility and combustibility as well as high volumetric energy density of \( \sim 1.86 \text{ kcal cm}^{-3} \), which creates a vast opportunity for its use as explosives and propellants [1, 2]. Fe$_2$O$_3$ is a widely used low cost oxidizer possessing good oxygen donation ability as well as catalytic effects on reactivity of energetic materials. Previous studies [3, 4] showed that Fe$_2$O$_3$ could be used to improve the combustion performance of Zr particles. Though these studies proposed that coating Zr particles with Fe$_2$O$_3$ was a good way to exert the promoting effect of Fe$_2$O$_3$ on combustion process, it is difficult to obtain such composite particles on a large scale. Directly mixing different components of energetic materials such as Fe$_2$O$_3$ and Zr particles may still be the most practical way currently [5]. However, nanometer particles often have the difficulty in uniform dispersion, though they are expected to have better performances than the micrometer particles. In recent years, micro-sized metal-oxide particles having nanometer building blocks and porous structure are gradually perceived to be potentially more advantageous than corresponding nano-sized metal-oxides in many fields. Jian [6] demonstrated that hollow CuO spheres of large particle sizes had better performance than the commercial small-sized nanometer CuO particles in CuO/Al thermite. Chandru [7] prepared nano-structured Fe$_2$O$_3$ catalysts with particle sizes of several hundred micrometers and showed that these Fe$_2$O$_3$ had better catalytic performance in the combustion of AP-based composite propellant as compared with the small-sized nano Fe$_2$O$_3$ rod. Bezmenitsyn [8] showed that thermites composed of mesoporous Fe$_2$O$_3$ and Al nano-particles exhibited suitable characteristics as an excellent propellant initiator. Chen [9] found that large-sized sea-urchin shape MnO$_2$ with hierarchical structure had better catalytic effects than the small-sized linear n-MnO$_2$ on
thermal decomposition of AP. Hu [10] compared the catalytic performance of hollow mesoporous CuO microspheres with solid nano-CuO and micro-CuO particles on decomposition of AP, and confirmed the better performance of hollow mesoporous CuO microspheres than others. The superior performance of porous micro-particles composed of nano-sized assembly particles can be generally ascribed to the following two aspects. (1) Porous structure favors the large surface area and thus large interfacial contact areas between metal oxides and other components, and then shortens heat and mass transfer distance during reaction [11]; (2) Reasonable porous structure provides more pathways for the convective propagation [12, 13] of the reaction energy. Therefore, micro-sized metal oxides having nano-sized assembly blocks and porous structure open up a new avenue to tailoring the performance of energetic materials.

Among various methods to prepare porous structured micro-sized metal oxides, metal-organic frameworks (MOF)-templating is an effective approach. MOF-derived metal oxides easily have large surface area, high porosity and adjustable morphology [14–16], providing diverse means for their performance tailoring. However, MOF-derived metal oxides have rarely been studied as oxidizers in energetic materials [17, 18].

In this work, MOF-derived Fe₂O₃ is synthesized and examined as the oxidizer in Fe₂O₃/Zr system. Performance of MOF-derived Fe₂O₃ is compared with commercial nanometer Fe₂O₃ (named as n-Fe₂O₃) in terms of thermal behavior and combustion characteristics of Fe₂O₃/Zr mixtures. Possible mechanisms in combustion reactions for Fe₂O₃/Zr mixtures containing different Fe₂O₃ are analyzed.

2. Experimental

Fe₂O₃ was synthesized by using MIL-53(Fe) as the template and a calcination treatment. MIL-53(Fe)-derived Fe₂O₃ was prepared by referencing previous work by Banerjee [19]. In detail, 1.35 g FeCl₃·6H₂O and 0.83 g H₂BDC were added into 25 ml DMF and magnetically stirred for 30 min at room temperature. Then the solution was transferred into an autoclave of 100 ml, and kept at 150 °C for 2 h. After cooling down to room temperature a rust-colored precipitate was obtained, which was then separated by centrifugation. As-obtained product was washed with deionized water, followed by centrifugation to separate the solid phase. After repeating the washing and centrifugation processes for four times, the color of the solid phase turned into light-yellow. The resulted light yellow solid phase was dried at vacuum at 80 °C for 18 h to remove the residual solvent and water. Finally, the precursor was calcined at different temperatures to obtain Fe₂O₃ with different microstructures. The phase structure and the morphology of the precursor before and after calcination were characterized by XRD and SEM, respectively. TG test was conducted to help determine the proper calcination temperature of the precursor.

As-obtained Fe₂O₃ were evenly mixed with Zr powders (particle sizes of mesh 400) to obtain Fe₂O₃/Zr mixture (weight ratio of 45:55) with a mortar and pestle. Thermal behavior of Fe₂O₃/Zr mixture in air atmosphere was examined by differential scanning calorimetry (DSC) technique at a heating rate of 10 K min⁻¹. Combustion characteristics of Fe₂O₃/Zr mixtures were evaluated by measuring the optical emission signal of the sample with a fiber optic spectrometer (Ocean Optics HR4000 CG-UV-NIR) and a Si detector (Thorlabs, DET 10 A) combined with an oscilloscope (Tektronix 4054B). The schematic experimental setup was shown in figure 1, in which the loose powder sample was placed in the groove inside the sample holder, and ignited by a NiCr hotwire with diameter of 0.5 mm. For each test, the resistance of the NiCr hotwire was kept to be ~0.6 Ω by fixing the length of the hotwire, and the current employed was 10 A. The heating rate was ~660 K s⁻¹. The morphology and composition of Fe₂O₃/Zr mixtures as well as their combustion products were characterized by SEM-EDS and XRD. For reference, commercial nano-Fe₂O₃ having an averaged particle size of 30 nm was used to compare with MOF-derived Fe₂O₃. n-Fe₂O₃ powders were first ultrasonically dispersed in ethanol, and then wetly mixed with Zr powders until ethanol was evaporated.
3. Results and discussions

3.1. Characterization of materials

XRD pattern of the as-synthesized MIL-53(Fe) precursor is shown in figure S1(a) (available online at stacks.iop.org/MRX/8/105014/mmedia). The diffraction peaks are consistent with the simulation pattern of MIL-53(Fe), indicating that MIL-53(Fe) is successfully synthesized. SEM image of as-synthesized MIL-53(Fe) is shown in figure S1(b). It is seen that most of the MIL-53(Fe) particles have trigonal column-like morphologies, and the averaged particle size is \( \sim 100 \mu m \). To determine the transformation temperature from MIL-53(Fe) to Fe\(_2\)O\(_3\), TG test was conducted. The TG result (figure S2) shows that the pyrolysis temperature of MIL-53(Fe) should be higher than 420 °C. Therefore, two calcination temperatures, i.e. 450 °C and 550 °C were selected to tune the microstructure of as-obtained Fe\(_2\)O\(_3\). Corresponding products are named as 450 °C-Fe\(_2\)O\(_3\) and 550 °C-Fe\(_2\)O\(_3\), respectively.

Figure 2 shows comparison of XRD patterns of MIL-53(Fe)-derived Fe\(_2\)O\(_3\) with commercial n-Fe\(_2\)O\(_3\). It is seen that 450 °C-Fe\(_2\)O\(_3\) and 550 °C-Fe\(_2\)O\(_3\) show sharp diffraction peaks within 30°~70°, which are identified to the phase of \( \alpha \)-Fe\(_2\)O\(_3\). In addition, an amorphous halo peak presents at around 20° for each sample, which is more obvious for 450 °C-Fe\(_2\)O\(_3\). By referencing the XRD pattern of MIL-53(Fe), this amorphous peak is attributed to the incomplete pyrolysis of MIL-53(Fe). Diffraction peaks of n-Fe\(_2\)O\(_3\) are wider than that of MIL-53(Fe)-derived Fe\(_2\)O\(_3\), indicating that the crystallinity of the former is poorer.

Figure 3 shows SEM images of n-Fe\(_2\)O\(_3\), 450 °C-Fe\(_2\)O\(_3\) and 550 °C-Fe\(_2\)O\(_3\). It is observed that n-Fe\(_2\)O\(_3\) powders agglomerate seriously, though the nominal particle size is \( \sim 30 \) nm. The sizes of n-Fe\(_2\)O\(_3\) agglomerations range from several \( \mu m \) to \( \sim 15 \mu m \). The particle sizes and morphologies of MOF-derived Fe\(_2\)O\(_3\) change with the calcination temperature of MIL-53(Fe). 450 °C-Fe\(_2\)O\(_3\) particles mainly show trigonal prism-like porous morphologies (high-magnification SEM images can be seen in figure S3), and the averaged particle size is above 20 μm. Some irregular-shaped small particles of \( \sim 5 \mu m \) can also be seen to scatter around or on the surfaces of those regular-shaped large particles. Those large regular particles are composed of a huge number of nanometer particles, and many pores and cracks can be seen on the surfaces of particles. 550 °C-Fe\(_2\)O\(_3\) particles also present trigonal prism-like outer shapes, but the averaged particle size increases to \( \sim 50 \mu m \). What’s more, the surfaces of particles seem less porous, which should be due to sintering of the assembly particles. (high-magnification SEM images can be seen in figure S4).

Figure 4 shows SEM images of Fe\(_2\)O\(_3\)/Zr mixtures containing different Fe\(_2\)O\(_3\) particles. EDS result (seen in figure S5) confirms that the large particles in figures 4(a)–(b) are composed of Fe\(_2\)O\(_3\) and Zr. Figures 4(a)–(b) show that n-Fe\(_2\)O\(_3\) particles agglomerated and wrapped around Zr particles after mixing process. However, figures 4(c)–(d) and figures 4(e)–(f) showed that MOF-derived micrometer porous Fe\(_2\)O\(_3\) particles were broken into small fragments after mixing process. These small fragments also wrapped around Zr particles and had good dispersions in the mixture. Moreover, from the enlarged images of fragments shown in figures 4(e) and (f), it was found that the inside stacking structure of 450 °C-Fe\(_2\)O\(_3\) and 550 °C-Fe\(_2\)O\(_3\) particles was different. The inside of 550 °C-Fe\(_2\)O\(_3\) particles seemed more porous, and the sizes of primitive assembly blocks were smaller in comparison to 450 °C-Fe\(_2\)O\(_3\).
3.2. Thermal behavior of Fe$_2$O$_3$/Zr

To examine effects of the type of Fe$_2$O$_3$ on thermal behavior of Fe$_2$O$_3$/Zr mixture heated in air, DSC curves of three mixtures are compared, and TG-DSC curves of pure Zr powders are given for reference. It is seen from figure 5(a) that an obvious weight gain of pure Zr powders begins from $\sim 250$ °C and ends at around 800 °C, accompanied by a broad exothermic peak centering at 613.5 °C. This corresponds to the oxidization of Zr powders by air. Figure 5(b) shows that each Fe$_2$O$_3$/Zr sample has one broad exothermic peak. The exothermic onset temperatures of three Fe$_2$O$_3$/Zr mixtures resemble that of pure Zr, which are significantly lower than the thermal decomposition temperature of pure Fe$_2$O$_3$ ($\sim 1100$ °C). This indicates that thermal reaction of
Fe$_2$O$_3$/Zr mixture should be initiated by air-oxidation of Zr component rather than the oxygen released by Fe$_2$O$_3$. On the other side, it is noted that the exothermic peaks of Fe$_2$O$_3$/Zr mixtures are also much lower than the decomposition temperature of pure Fe$_2$O$_3$, which reveals that the exothermic reaction of Fe$_2$O$_3$/Zr mixture involves solid-solid reaction between Fe$_2$O$_3$ and Zr \cite{20}. However, the differences in temperatures and areas of exothermic peaks for different Fe$_2$O$_3$/Zr mixtures are very small, suggesting no obvious dependences on the particle size and morphology of Fe$_2$O$_3$. One possible reason is that the test is conducted in air atmosphere and with a low heating rate, in which case the dominated reaction is the oxidation of Zr powders by air due to the high reactivity of Zr.

3.3. Combustion characteristics of Fe$_2$O$_3$/Zr thermite

Combustion tests under high heating rates were conducted to further examine the influence of different Fe$_2$O$_3$ on reaction characteristics of Fe$_2$O$_3$/Zr mixtures. Figure 6 shows optical emission spectra and temporal evolutions of optical emission intensity during combustion of different Fe$_2$O$_3$/Zr mixtures. It is necessary to point out that collection of the optical emission spectrum of n-Fe$_2$O$_3$/Zr mixture failed under the same testing distance, which was because the optical emission intensity was so weak that the signal could not be detected by the spectrometer. Optical emission spectra (figure 6(a)) of MOF-derived Fe$_2$O$_3$/Zr are continuum spectra on
which two impurity peaks (Na atoms at ∼589 nm and K atoms at 766 nm) are superimposed. Therefore, the combusting sample can be approximately viewed as a greybody, and the intensity of the optical emission in figure 6(a) can be interpreted as an indicative of the flame temperature. It is concluded that 550 °C-Fe₂O₃/Zr mixture has a higher flame temperature than that of the 450 °C-Fe₂O₃/Zr mixture. Temporal evolutions of optical emission intensities in figure 6(b) further reveal that n-Fe₂O₃/Zr mixture has the lowest flame temperature among the three samples, though their combustion times are similar.

These results confirm that the size and microstructure of Fe₂O₃ indeed have an obvious influence on combustion characteristics of Fe₂O₃/Zr mixtures under high heating rates. This is different from the case of heating Fe₂O₃/Zr at low heating rates like DSC tests.

Figure 7 shows XRD patterns of condensed combustion products of different Fe₂O₃/Zr mixtures. The major composition of n-Fe₂O₃/Zr after combustion is ZrO₂, Fe and some unreacted Zr, suggesting that the combustion is not complete. The combustion products of Fe₂O₃/Zr containing MOF-derived Fe₂O₃ are mainly composed of ZrO₂ and Fe, which is corresponding to the complete redox reaction between Fe₂O₃ and Zr. Besides, there is a small impurity peak presented at ∼30° for each sample. This is probably resulted from the oxidation products (NiCr₂O₄, PDF #23–0432) of NiCr hotwire used for ignition.

Figure 8 shows SEM images of combustion products of different Fe₂O₃/Zr mixtures. It is clearly observed that morphologies of three samples differ significantly. Combustion products of n-Fe₂O₃/Zr (figures 8(a)–(b)) show two distinct sizes and morphologies. One is the very large spherical particles of ∼30 μm, which is far larger than the scale of both n-Fe₂O₃ agglomerations and Zr particles. The other is similar with the n-Fe₂O₃/Zr mixture before combustion, indicating that combustion reaction is not complete, which is in accordance with XRD results in figure 7. On contrary, combustion products of MOF-derived Fe₂O₃/Zr (figures 8(c)–(f)) are
Nearly only composed of large scale spherical particles. Compared with 450 °C-Fe₂O₃, 550 °C-Fe₂O₃ results in larger sized spherical combustion products. The enlarged images show that these spherical particles are hollow, implying that interior expansion or explosion may have occurred [21, 22].

Based on previous studies on micro-explosion phenomenon of Zr particles [21–23] and the condensed state reaction mechanisms of thermites at high heating rates [24], formation process of the observed large spherical products is explained as follows. For each Fe₂O₃/Zr mixture, ignition is initiated by the air-oxidization of Zr component, and the combustion reactions become self-sustaining when local solid-solid reaction between Zr and Fe₂O₃ occurs at the contact interface. Oxidation of Zr particles proceeds inward from the surface due to the diffusion of oxygen across the Zr/ZrO₂ interface, producing core–shell structure particles with ZrO₂ as the shell and Zr as the core. At the same time, the Zr core and the ZrO₂ shell are heated rapidly by the released reaction heat. By referencing the maximum combustion temperature of Fe₂O₃/Zr (≈2380 °C) [4] and Zr particles (≈2827 °C) [25], it is inferred that neither evaporation of Zr (boiling point: ≈4377 °C) nor evaporation of ZrO₂ (boiling point: ≈4300 °C) shell can occur, but melting of Zr (melting temperature: ≈1852 °C) is possible. Due to the difference in thermal expansion coefficients of ZrO₂ shell and Zr core, the ZrO₂ shell will burst, resulting in the outward splashing of melted Zr from the cracks on particle surface. These splashed liquid Zr drops are violently oxidized when exposure to oxygen (either from the oxygen in air or from the oxygen provided by Fe₂O₃), forming large spherical particles with new ZrO₂ shell.

According to the above analysis, the difference in combustion performance of different Fe₂O₃/Zr mixtures should be resulted from the difference in the degree of solid–solid reaction at contact interfaces of Fe₂O₃ with Zr, as is schematically illustrated in figure 9. The serious agglomeration of n-Fe₂O₃ particles impedes the intimate contact of n-Fe₂O₃ with Zr particle and thus oxygen transport from Fe₂O₃ to Zr particles [26], so solid-solid reaction of them occurs locally, resulting in low heat release and low flame temperature. Therefore, the melting and splashing of Zr particle are difficult (figure 9(a)). The whole combustion process of n-Fe₂O₃/Zr is probably dominated by the interface diffusion-controlled solid–solid reaction. However, MOF-derived Fe₂O₃ particles have larger contact areas with Zr particles because most of them are broken into dispersed primitive nanometer particles during mixing with Zr particles, which enables the multi-point solid–solid reactions at Fe₂O₃/Zr interfaces, resulting in a large amount of heat release and ultra-high temperature rise of reactants (figure 9(b)).

The ultra-high temperature rise not only accelerates the thermal decomposition of Fe₂O₃ to release gas oxygen, but also leads to the melting and splashing of most Zr particles. Consequently, the reaction mechanism of subsequent combustion of Zr has become beyond the solid–solid state reaction between Fe₂O₃ and Zr. Compared with 450 °C-Fe₂O₃/Zr, the combustion performance of 550 °C-Fe₂O₃/Zr is better. This is probably due to the superior crystallinity and porous structure of 550 °C-Fe₂O₃, which favor the oxygen transport along grain boundaries [5].

Figure 8. SEM images of combustion products of different Fe₂O₃/Zr thermites: (a)–(b) n-Fe₂O₃/Zr (c)–(d) 450 °C-Fe₂O₃/Zr (e–f) 550 °C-Fe₂O₃/Zr.
4. Conclusions

MOF-derived micrometer porous Fe₂O₃ particles are demonstrated to be a more efficient oxidizer than commercial nanometer Fe₂O₃ for Fe₂O₃/Zr system. Thermal behaviors of Fe₂O₃/Zr mixture containing MOF-derived Fe₂O₃ and nano-Fe₂O₃ have little difference when heated in air atmosphere with the low rate of 10 K min⁻¹. However, particle size and microstructure of Fe₂O₃ have an obvious influence on combustion characteristics of Fe₂O₃/Zr mixture at the high heating rate of ~660 K s⁻¹. MOF-derived Fe₂O₃ enables Fe₂O₃/Zr mixture to have more complete reactions and higher flame temperatures than commercial nanometer Fe₂O₃. This is ascribed to the larger contact areas between fragments of MOF-derived Fe₂O₃ particles and Zr, which significantly increases the degree of solid-solid exothermic reaction at Fe₂O₃/Zr interfaces. MOF-derived Fe₂O₃ particles obtained at calcination temperature of 550 °C display the best performance due to their superior crystallinity and porous structure to other Fe₂O₃. Micrometer-sized porous metal oxide particles having nano-sized building blocks may be a better choice than those nanometer counterparts for applications as the oxidizer in thermites.

Acknowledgments

Thanks for the support of National Natural Science Foundation of China (No. 51876195) and Science and Technology Research Foundation of Sichuan Province (No. 2021YFG0016, 2018JY0476).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Xiaoli Kang  @  https://orcid.org/0000-0002-4096-7473

References

[1] Lempert D B, Nechiporenko G N and Manelis G B 2011 Energetic capabilities of high-density composite solid propellants containing zirconium or its hydride Combust. Explo. Shock. 47 45–54
[2] Nagarkar A G, Bora B, Thosar R B, Shirwalkar S V, Shelkar H, Nath T and Asthana S 2012 Study on a system with a neutral barrier for high explosives and a zirconium-based solid incendiary Propell. Explos. Pyrot. 37 713–7
[3] Wang Q H, Sun J H, Deng J, Wen H and Xu Y 2015 Combustion behavior of Fe$_2$O$_3$-coated zirconium particles in air Energy Procedia 66 269–72
[4] Lv B, Yao X, Hou B, Dong W and Sun Y 2008 Preparation and combustion properties of α-Fe$_2$O$_3$ coated Zr particles Mater. Res. Bull. 43 2769–77
[5] Han B H, Kim Y, Jang S, Yoo J and Yoh Jack J 2019 Thermochemical characterization of Zr/Fe$_2$O$_3$ pyrotechnic mixture under natural aging conditions J. Appl. Phys. 126 105113
[6] Jian G, Liu L and Zachariah M R 2015 Facile aerosol route to hollow CuO spheres and its superior performance as an oxidizer in nanoenergetic gas generators Adv. Funct. Mater. 23 1341–6
[7] Chandru R A, Patel R P, Oommen C and Raghunandan B N 2019 Initial studies on development of high-performance nano-structured Fe$_2$O$_3$ catalysts for solid rocket propellants J. Mater. Eng. Perform. 28 810–6
[8] Bezmelitsyn A, Thiruvengadathan R, Barizuddin S, Tappmeyer D, Apperson S, Gangopadhyay K and Gangopadhyay S 2010 Modified nanoenergetic composites with tunable combustion characteristics for propellant applications Propell. Explos. Pyro. 35 384–94
[9] Chen Y, Ma K F, Wang J X, Gao Y, Zhu X F and Zhang W C 2018 Catalytic activities of two different morphological nano-MnO$_2$ on the thermal decomposition of ammonium perchlorate Mater. Res. Bull. 101 56–60
[10] Hu Y H, Yang S M, Tao B W, Liu X L, Lin K F, Yang Y L, Fan R Q, Xia D B and Hao D H 2019 Catalytic decomposition of ammonium perchlorate on hollow mesoporous CuO microspheres Vacuum 159 105–11
[11] Wang N, Hu Y, Ke X, Xiao L, Zhou L, Peng S S, Hao G Z and Jiang W 2020 Enhanced-absorption template method for preparation of double-shell NiO hollow nanospheres with controllable particle size for nanothermite application Chem. Eng. J. 379 122330
[12] Shin D J, Kim W D, Lee S and Lee D C 2018 Nanothermite of Al nanoparticles and three-dimensionally ordered macroporous CuO: mechanistic insight into oxidation during thermite reaction Combust. Flame 189 87–91
[13] Wang J, Zheng B, Qiao Z Q, Chen J, Zhang L Y, Zhang L, Li Z Q, Zhang X Q and Yang G C 2018 Construct 3D porous hollow Co$_3$O$_4$ micro-sphere: a potential oxidizer of nano-energetic materials with superior reactivity Appl. Surf. Sci. 442 767–72
[14] Xu X D, Cao R G, Jeong S and Cho J 2012 Spindle-like mesoporous α-Fe$_2$O$_3$ anode material prepared from MOF template for high-rate lithium batteries Nano Lett. 12 4988–91
[15] Wang M J, Hou T Y, Shen Z R, Zhao X D and Ji H M 2019 MOF-derived Fe$_2$O$_3$: phase control and effects of phase composition on gas sensing performance Sensor Actu. B-Chem. 292 171–9
[16] Mo R X, Han D Q, Yang C W, Tang J Y, Wang F and Li C L 2021 MOF-derived porous Fe$_2$O$_3$ nanocubes combined with reduced graphene oxide for n-butanol room temperature gas sensing Sensor. Actu. B-Chem. 330 129326
[17] He W, Ao W, Yang G C, Yang Z J, Guo Z Q, Liu P J and Yan Q L 2020 Metastable energetic nanocomposites of MOF-activated aluminum featured with multi-level energy releases Chem. Eng. J. 381 122623
[18] He W, Li Z H, Chen S W, Yang G C, Yang Z J, Liu P J and Yan Q L 2020 Energetic metastable n-Al@P/VDF/EMOF composite nanofibers with improved combustion performances Chem. Eng. J. 383 123146
[19] Banerjee A, Aravindan V, Bhatnagar S, Mhamane D, Madhavi S and Ogale S 2013 Superior lithium storage properties of α-Fe$_2$O$_3$ nano-assembled spindles Nano Energy 2 890–6
[20] Ewald K H, Anselmi-Tamburini U and Munir Z A 2000 Combustion of zirconium powders in oxygen Mater. Sci. Eng. A 291 118–30
[21] Wainwright E R, Lakshman S V, Leong A F T, Kinsey A H, Gibbins J D, Arlington S Q, Sun T, Fezzaa K, Hufnagel T C and Wehls T P 2019 Viewing internal bubbling and microexplosions in combusting metal particles via x-ray phase contrast imaging Combust. Flame 199 194–203
[22] Wainwright E R, Schmauss T A, Lakshman S V, Overdeep K R and Wehls T P 2018 Observations during Al:Zr composite particle combustion in varied gas environments Combust. Flame 196 487–99
[23] Yu J L, Zhang X Y, Zhang Q, Wang L B, Ji K, Peng L and Gao W 2016 Combustion behaviors and flame microstructures of micro- and nano-titanium dust explosions Fuel 181 785–92
[24] Jacob R J, Jian G Q, Guerieri P M and Zachariah M R 2015 Energy release pathways in nanothermites follow through the condensed state Combust. Flame 162 258–64
[25] Badiola C and Dreizin E L 2013 Combustion of micron-sized particles of titanium and zirconium P Combust. Inst. 34 2237–43
[26] Sullivan K T, PiekieI N W, Wu C, Chowdhury S, Kelly S T, Hufnagel T C, Fezzaa K and Zachariah M R 2012 Reactive sintering: an important component in the combustion of nanocomposite thermites Combust. Flame 159 2–15