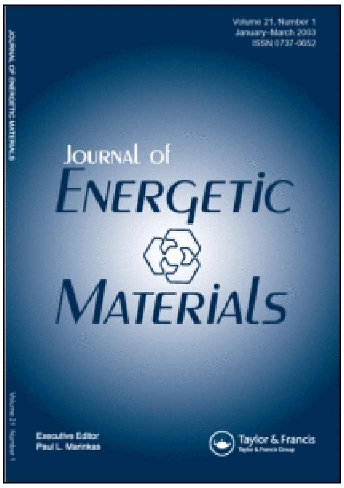

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Stability and Degradation Processes of Pentaerythritol Tetranitrate (PETN) on Metal Oxide Surfaces

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The chemical stability of pentaerythritol tetranitrate (PETN) when placed in physical contact with metal oxides is investigated. In this study, PETN was placed on the surfaces of a range of microcrystalline metal oxides including MnO_2, *CuO*, MoO_3, WO_3, Bi_2O_3, SnO_2, *and* Fe_2O_3 *in coverages of 1–3.5 monolayers by a wet impregnation technique. Samples were then placed in a controlled temperature environment at 50°C and checked periodically for the presence of decomposition products using liquid chromatography. PETN proved to be inert over all of the oxides except* MoO_3, *which showed the relatively rapid evolution of a brown gas over a period of 48 h. Analysis of the evolved gas indicated that it is primarily* NO_2 *along with* N_2O_4, N_2O, *and* CO_2.

Keywords: composite, degradation, oxide, PETN, stability, surface chemistry

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Introduction

Recently, a new approach to the fabrication of high-output explosives and pyrotechnics has been developed that involves the use of binary inorganic solid-state reactive materials in combination with traditional organic high explosives such as 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-1,3,5-trinitramine (RDX), 1,3,5,7-tetramethylene-1,3,5,7-tetranitramine (HMX), and pentaerytritol tetranitrate (PETN). The binary inorganic materials are stoichiometric mixtures of metal (fuel) and metal-oxide (oxidant) particles that react through a highly exothermic redox reaction that is typified by the well-known thermite reaction (Eq. (1)).

$$\mathrm{Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe} \quad \Delta\mathrm{H} = 3.97\,\mathrm{kJ/g} \tag{1}$$

The advantage of these binary inorganic materials is that the energy density can be several times higher than that of conventional explosives. Traditionally, exploiting these materials has been problematic since the rate of energy release is usually significantly lower than that of traditional high-energy materials.

In order to overcome this problem, new composite materials have been developed in which the inorganic fuel/oxidant systems are mixed with conventional explosives (e.g., TNT, RDX, HMX and PETN). The energy release in these systems is driven by the conventional explosive, which drives the kinetics of the binary inorganic materials, thereby releasing energy much more rapidly and in a controlled fashion. Studies to date have indicated that this approach affords great promise in exploiting the high-energy density provided by binary inorganic energetic compositions. In the case of TNT it has been studied with various oxidant phases and fuels (e.g., MnO_2 and Al, Al–Zr and Mg–Al alloys) as high-energy-density explosives for high-penetration applications and as components for boosters and primers and, in fact, patents exist on this technology [1–3]. PETN, on the other hand, has been studied with binary inorganic reactive materials including Al, Al alloys, and Zr as fuels and Pb_3O_4, Fe_2O_3, and MnO_3 as the oxidants for their use as boosters and primers as well as their use as a laser initiated system [2,4].

One problem that exists in the incorporation of conventional organic high-energy materials with metal/metal-oxide binary compositions is the possibility for an inherent incompatibility between the organic and inorganic phases to occur. This incompatibility arises from deleterious surface chemistry between the organic and metal or metal-oxide phase in the composite. These deleterious processes arise from interfacial chemical processes including, but not exclusively, reduction at the surface of the metal (fuel) and oxidation at the oxide surface. The magnitude of these processes will likely be exacerbated by the degree of contact between the organic materials and the metal or metal-oxide surfaces and will be affected by temperature, humidity, and other ambient conditions of storage and handling.

In a previous study we have shown that TNT undergoes a thermal reaction on the surface of MnO_2 and CuO that suggests an inherent incompatibility with these oxides [5]. In this article we describe the results in a comprehensive study of the compatibility of pentaerythritol tetranitrate (PETN) when placed in physical contact with a range of metal oxides chosen based on their use or proposed use in composite energetic materials.

Experimental

Materials

MnO_2 (Aldrich, reagent grade, $>90\%$ purity, $\sim 10\,\mu m$ particle size), CuO (Aldrich, nanopowder, $\sim 33\,nm$), Fe_2O_3 (Fisher, anhydrous), MoO_3 (nano and micron, Climax Molybdenum), SnO_2 (Keeling & Walker Ltd.), WO_3 (Atlantic Equipment Engineering), and Bi_2O_3 (Aldrich), were used as received from the manufacturer. Pentaerythritol tetranitrate (PETN) was prepared according to the literature and was stored in acetone (Aldrich, HPLC grade) for safety [6]. Acetonitrile (Fisher, HPLC grade) and toluene (Aldrich, HPLC grade) were used as received.

Long-Term Surface Reactivity Studies

A wet impregnation technique was used in preparing the samples for the long-term reactivity studies. Two hundred and eight microliters of a PETN standard solution (~0.50 M) were diluted with 1 mL acetone and subsequently added to 1 g of the metal oxide. The acetone was removed under a vacuum (10^{-3} torr), leaving a dry powder containing the metal oxide and the PETN on its surface. The approximate coverage area of the PETN is 1543 m^2/g, which is based on the estimated area of a PETN molecule, assuming the molecule is a disk with the outer circumference defined by the oxygen atoms of the nitro groups (obtained from the crystal structure of PETN) with the radius extending from the central carbon atom.

The samples were placed in sealed containers and held at 50°C in an oven over a period of several months. Periodically, a small portion of the sample was removed (~0.10 g) and stirred into 1 mL of acetone. The solids were allowed to settle, and the supernatant was collected containing any organic species and analyzed by HPLC using a 65:35 CH_3CN/H_2O solution as the mobile phase and toluene as an internal standard. There was no evidence of new compounds in the chromatograph; however, a comparison between the control sample and each subsequent sample removed showed a decomposition of the PETN was occurring at the surface of the MoO_3. The percentage degradation was determined from the ratio of the integrated peak area of the PETN in the HPLC to that of the sum of all of the peak areas. For oxides that induced a significant amount of degradation, the products were analyzed using FT-IR spectroscopy.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q1000 Series DSC under O_2. Samples were prepared using the wet impregnation method as described above. An aliquot of 84 μL of a PETN standard solution (~0.5 M) was diluted with a small amount of acetone and added to 0.25 g of MoO_3 (both nano and micron sizes). The solvent was removed under a vacuum, and the dry powder containing the PETN on the surface of the metal oxide was then analyzed. Samples of pure PETN and PETN on the surface of silica gel and KBr were also analyzed to differentiate surface chemistry specific to the metal oxides.

Results and Discussion

Degradation Studies

The long-term degradation studies were designed to simulate long-term ambient storage conditions of multicomponent high-energy materials in direct contact with metal oxide surfaces. Relatively low concentrations (~1–3.5 monolayers) of PETN were deposited onto the oxide surfaces in order to isolate specific interfacial chemistry as well as to allow the sensitive detection of reaction products. Table 1 shows the oxides surveyed in the study and their PETN surface coverage in the prepared samples.

A chromatogram of the samples was taken immediately following preparation to establish the initial purity. The samples were then placed in a 50°C oven under ambient atmosphere and allowed to react over the course of a couple of months, with aliquots periodically being withdrawn for analysis using HPLC. The amount of decomposition over time of PETN for most oxide surfaces was found to be very small.

PETN proved to be inert or only slightly reactive on many of the metal oxide surfaces. The amount of PETN on the surface of Bi_2O_3, CuO, WO_3, Fe_2O_3, MnO_2, and SnO_2 remains

Table 1
Surface coverage of PETN on each metal oxide

Metal oxide	BET surface area (m^2/g)	PETN coverage (monolayers)
MnO_2	40.2477	2.0
CuO	31.9157	2.5
WO_3	17.0450	2.9
MoO_3 (large)	24.9929	2.0
MoO_3 (nano)	55.1272	0.91
Bi_2O_3	25.9291	3.1
SnO_2	21.3088	3.8
Fe_2O_3	32.9970	2.4

fairly constant over the period analyzed (~60 days) with only small changes in the concentration of PETN, which were within the experimental error of the measurement. However, PETN did show significant decomposition on the surface of MoO_3 as evidenced by a decline in the amount of PETN and the concomitant production of a brown gas, which can be observed visually in the sample container. Increasing the ambient temperature at which the sample is stored results in a more rapid production of the gas.

Reactivity of PETN with MoO_3

Thermal Analysis. Thermal analysis of pure pentaerythritol tetranitrate using differential scanning calorimetry (DSC) is shown in Fig. 1. The thermal scan shows a sharp endotherm at 141°C, which corresponds to the melting, and an exotherm, whose observed peak at this scan rate (10°/min) is at 205°C, corresponding to the decomposition of the molecule. When

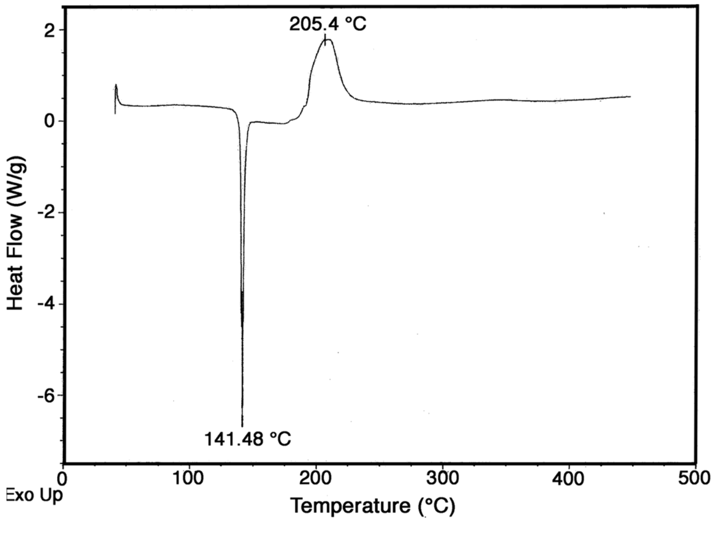
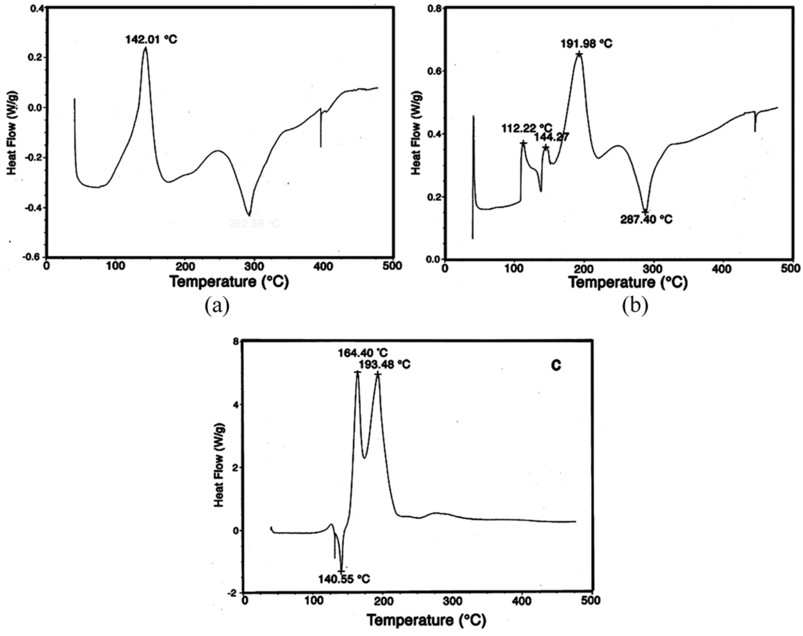


Figure 1. Differential scanning calorimetry (DSC) of pure PETN with a vented sample pan (note exothermic processes are above the baseline).

the sample is analyzed in a sealed container, the decomposition becomes a deflagration event with an abrupt release of energy. When considering composites of PETN with inorganic oxides, the effect of the inorganic–organic interface on these well-understood thermal processes is of interest. The DSC plot of PETN at ∼2 monolayer coverage on nanoscale MoO_3 is shown in Fig. 2. At slightly less than 2 monolayer coverage of PETN on MoO_3, decomposition occurs at a significantly lower temperature of 142°C, with no melting endotherm being observed. The lack of a melting endotherm is expected since there is no crystalline bulk phase present. When the coverage of PETN is increased slightly to approximately 2 monolayers, a melting endotherm begins to be observed at 138°C. The melting endotherm is superimposed on the middle of the



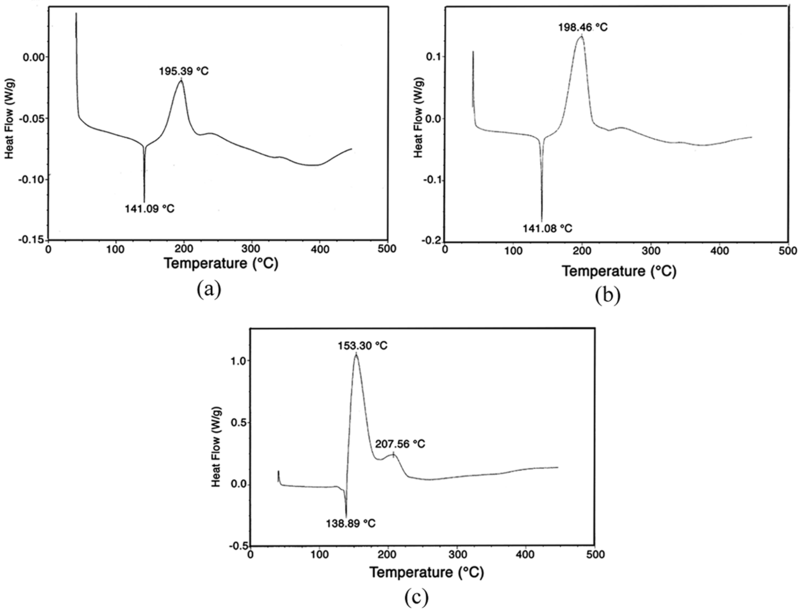
(a) (b)

(c)

Figure 2. DSC of (a) <2, (b) 2, and (c) 6 monolayer coverage of PETN deposited on nanoscale MoO_3.

broad decomposition exotherm, thereby splitting it into two apparent peaks at 112 and 144°C. There is also an exothermic process located at 192°C, which is lower than for the pure PETN presumably due to interfacial mediation at the surface of the oxide. An endotherm is also present at 292 and 287°C for the <2 and 2 monolayer samples, respectively, which likely represents a desorption of some of the products from the initial decomposition. A sample with excess PETN on the surface of MoO_3 shows an endotherm at 140.6°C and two exothermic processes, one whose peak is close to that resolved in the bulk (193°C), and a low-temperature exothermic process at 164°C. We interpret this as coming from the superposition of the interfacial and the bulk processes observable at the higher loadings of PETN, wherein the melting endotherm at 140.6°C, which is more pronounced at the higher loading, now dominates and obliterates most of the 141°C interfacial exotherm, leaving only a residual spike at 164°C. The size of the 164°C exotherm, however, is quite large; therefore, we cannot rule out a more complex surface-mediated decomposition process that results from the interfacial reactions with the melt. An endothermic process just below 300°C is not seen in the bulk sample as it is in the monolayer samples due to the fact that it may be attributed to a decomposition that occurs at the surface and is therefore solely an interfacial process.

The DSC data of PETN deposited on nanoscale MoO_3 is compared to that of PETN deposited on the larger micron-size MoO_3, which has a smaller surface area (Fig. 3). At a surface coverage of less than 2 monolayers, an endothermic process at 141°C, indicating the melt of PETN, is observed, as well as an exotherm at 195.4°C for the decomposition process. This exothermic process occurs at a lower temperature than that of the bulk PETN (205°C), showing that there is some interfacial mediation occurring; however, the fact that there is a melt present and only one decomposition peak indicates that there is mostly bulk crystalline phase present. In fact, similar processes are observed for the samples with a higher loading of PETN, showing that the same interfacial processes occurring on the



(a)

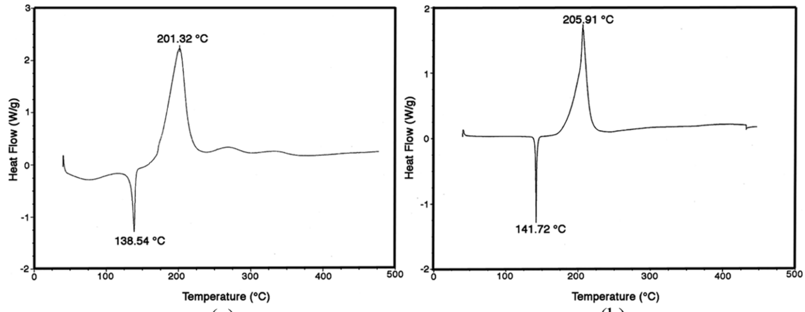
(b)

(c)

Figure 3. DSC of (a) <2, (b) 2, and (c) 6 monolayer coverage of PETN deposited on micron-scale MoO_3.

nanoscale MoO_3 do not also occur on the micron scale MoO_3. In short, when the surface area gets small enough, interfacial effects become less significant and are not observed in the thermal analysis or, alternatively, the large surface area provided by nanoscale materials will give rise to greater surface degradation effects. Comparable studies were performed on the remaining metal oxide surfaces, where a surface mediation effect was only observed at the surfaces of MnO_2 and CuO, which showed the decomposition peak occurring at a lower temperature than that of pure PETN (149 and 175°C, respectively).

It is important to determine whether the interfacial mediation of the decomposition temperature is specific to certain oxides or constituted a general surface effect. Thermal analysis of monolayers of PETN deposited on inert oxides and salts indicates that the decomposition temperature is not modified on all surfaces (Fig. 4). On fumed silica the decomposition



(a) (b)

Figure 4. DSC traces of PETN deposited on (a) SiO_2 and (b) KBr.

temperature is very similar to that of bulk PETN at 201°C. On simple salts such as KBr, there is also no detectable change in the decomposition temperature from that of the bulk. Thus, the interfacial effect is not a general effect but rather a specific interaction that occurs between PETN and the surface of nanoscale MoO_3.

While these results do not provide a chemical rationale for the interfacial effect, nor do they provide any specifics on the decomposition pathway(s) on the surface. It is clear from the thermal analysis that there is a significant surface reaction with MoO_3. This effect might well mitigate energy release processes or affect long-term stability of heterogeneous composite mixtures.

Product Analysis. The reaction processes of pentaerythritol tetranitrate (PETN) deposited on the surface of molybdenum (VI) oxide were studied using liquid chromatography and Fourier transform infrared spectroscopic techniques. The HPLC study was conducted over a period of 3 months wherein small aliquots of the sample were removed periodically for analysis. The chromatograph shows a modest (1.3%) decrease in the amount of PETN present after 21 days; however, no additional peaks in the chromatogram that might represent decomposition products are observed. This suggests that the primary decomposition products are likely gaseous species that diffuse out of the solid. Only a small amount of net decomposition is observed chromatographically, which suggests that the reaction is localized at the interface and the catalytic decomposition of the bulk does not occur, at least at the temperatures studied.

The sample for the gas-phase FT-IR study was prepared as described previously. The container holding the sample was connected to a gas-phase IR cell that had previously been evacuated. The sample was set to heat to 100°C, and spectra were periodically recorded over a period of 2 days (Fig. 5). Peaks associated with the decomposition of PETN began to appear during the first hour of heating. The products observed by FT-IR were NO_2 (1629, 1597 cm^{-1}), N_2O_4 (1743 and 1270 cm^{-1}), N_2O (2236, 2212 cm^{-1}), and CO_2 (2359, 2342, and 3727–3600 cm^{-1}) [7]. The band occurring at 2918 cm^{-1} is due to the grease from the stopcocks of the gas cell heating slightly during the reaction and releasing a small amount of the grease into the cell. The band at 1270 cm^{-1} has been

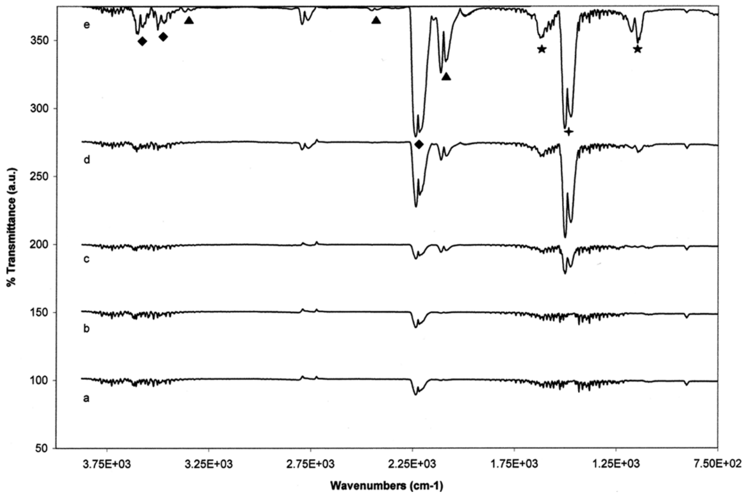


Figure 5. FT-IR spectroscopy of PETN on the surface of MoO_3 at 100°C after (a) 1, (b) 5, (c) 24, (d) 27.5, and (e) 46 h (◆ = CO_2, ▲ = N_2O, ★ = N_2O_4, ✦ = NO_2).

assigned to N_2O_4, which is in accordance with the reported values found by Mélen et al. [8]. However, this band seems to overlap with other fundamental vibrational bands of NO_2 as well as N_2O, which are at 1320 and 1285 cm^{-1}, respectively. A control sample of the MoO_3 without PETN prepared for FT-IR analysis showed that none of the products found were from the surface of the MoO_3 alone.

Conclusions

From the standpoint of compatibility, it is clear that the interfacial chemistry between PETN and inorganic surfaces can be pronounced. As indicated by the thermal analysis studies, at one level, this involves changes in the normal thermal decomposition pathways of the molecule, which may or may not have a net effect on stability or energy release in bulk composite materials. For redox active metal oxide phases, the interfacial processes can result in a net chemical reaction that will slowly convert PETN into another species and possibly into degradation products. For the specific oxides reported here, the surface interactions of PETN with MoO_3 produce a gas containing NO_2, N_2O, N_2O_4, and CO_2 species. Clearly, this result indicates that in composite energetic materials containing forms of MoO_3, the PETN will be changing over time, which suggests that stability and energy release may also be variable.

Acknowledgment

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