



## REVIEW

# A review on the use of nanometals as catalysts for the thermal decomposition of ammonium perchlorate

Shalini Chaturvedi, Pragnesh N. Dave \*

Department of Chemistry, Kachchh University, Bhuj 370001, India

Received 14 October 2010; accepted 20 May 2011

Available online 30 May 2011

### KEYWORDS

Ammonium perchlorate;  
Thermal decomposition;  
Nanoparticles;  
Metal;  
Alloys;  
Catalytic activity

**Abstract** In this review, an attempt to collect summarized literature data on catalytic effect of nanosized metals and nanoalloys on the thermal decomposition of ammonium perchlorates (AP) is made. Several experimental results show nanometals are more effective catalysts as compared to nanosized metal oxides. During decomposition process; metal react with oxygen containing species that are produced in decomposition process; and metal oxide is formed with large amount of heat which enhances the catalytic activity of metals as compared to metal oxide nanoparticles.

© 2011 King Saud University. Production and hosting by Elsevier B.V.  
Open access under [CC BY-NC-ND license](#).

### Contents

|  |     |
|--|-----|
| 1. Introduction . . . . .                        | 136 |
| 2. Transition metals as catalyst. . . . .        | 136 |
| 3. Metal alloys . . . . .                        | 137 |
| 4. Ammonium perchlorate . . . . .                | 137 |
| 4.1. Synthesis . . . . .                         | 137 |
| 4.2. Properties. . . . .                         | 137 |
| 4.3. Mechanism of thermal decomposition. . . . . | 138 |
| 4.3.1. Electron transfer mechanism . . . . .     | 138 |

\* Corresponding author.

E-mail address: [pragneshdave@gmail.com](mailto:pragneshdave@gmail.com) (P.N. Dave).

1319-6103 © 2011 King Saud University. Production and hosting by Elsevier B.V. Open access under [CC BY-NC-ND license](#).

Peer review under responsibility of King Saud University.

doi:10.1016/j.jscs.2011.05.009



Production and hosting by Elsevier

|  |     |
|--|-----|
| 4.3.2. Proton transfer mechanism . . . . .                             | 138 |
| 4.4. Solid rocket propellants. . . . .                                 | 139 |
| 5. Effect of metal and alloys on thermal decomposition of AP . . . . . | 140 |
| 6. Conclusion . . . . .  | 147 |
| Acknowledgments . . . . .  | 147 |
| References . . . . .   | 147 |

## 1. Introduction

The nanosciences have recently evolved as a major research direction of our modern society resulting from an ongoing effort to miniaturize at the nanoscale processes that currently use microsystems. Towards this end, it is well admitted that the bottom-up approach should now replace the classic top-down one, a strategic move that is common to several areas of nanosciences including opto-electronics, sensing, medicine and catalysis (Edwards et al., 2000; Feldmann and Jungk, 2001; Fievet et al., 1989; Saravanan et al., 2001; Vinod et al., 1998). The latter discipline certainly is the key one for the development of starting chemicals, fine chemicals and drugs from raw materials. Exciting new opportunities are emerging in the field of catalysis based on nanotechnology approaches. A new understanding and mastery of catalysis could have broad social impacts, since about 80% of the processes in the chemical industry depend on catalysts to work efficiently. Efforts in surface science have led to the discovery of new heterogeneous catalysts, however, until recently the only way to develop new or improved catalysts was by empirical testing in trial-and-error experiments. This time-consuming and costly procedure is now rapidly being replaced by rational design methods that utilize fundamental knowledge of catalysts at the nanoscale (Baumer and Freund, 1999; Gleiter, 1995; Rodriguez et al., 2002; Singh et al., 2009a,b,c; Trudeau and Ying, 1996; Valden et al., 1998). The advent of nanoscience and nanotechnology is providing the ability to create controlled structures and geometries to investigate and optimize a broad range of catalytic processes. As a result, researchers are obtaining fundamental insight into key features that influence the activity, selectivity, and lifetime of nanocatalysts. Materials reduced to the nanoscale can show different properties compared to what they exhibit on a nanoscale, enabling unique applications (Biju and Abdul Khader, 2003; Edelstein and Cammarata, 1998; Fernandez-Garcia et al., 2004; Lw et al., 2004; Tao and Wei, 2004). In the past two decades, the synthesis of metal nanoparticles received considerable attention due to their unusual properties and potential applications in optical, electrical catalytic, magnetic and so on. Ni nanoparticles have been prepared by polyol process (Chen and Hsieh, 2000), microemulsion process (Kurihara et al., 1995), while Ni, Co nanoparticles by hydrogen plasma method.

In material science, the range of properties of metallic systems can be greatly extended by taking mixtures of elements to generate intermetallic compounds and alloys (Ferrando et al., 2008). The rich diversity of compositions, structures and properties of metallic alloys has led to widespread applications in electronic and catalysis. To fabricate materials with well defined, controllable properties and structures on the nanometer scale, afforded by intermetallic materials has generated interest in bimetallic nanoalloys. Surface structures, composi-

tion and segregation properties of nanoalloys are of interest as they are important in determining chemical reactivity especially the catalytic activity. Moreover, nanoalloys are also of interest as they may display structures and properties which are distinct from those of the pure elemental cluster and bulk alloys. Nanoalloys have been prepared by low temperature synthetic pathway, co-decomposition, co-reduction methods etc. (Ferrando et al., 2008).

When the average diameter of particle is less than 100 nm, the particle will possess many interesting properties, such as large specific area, little size effect and quantum size effect (Buzea et al., 2007). Thus, the addition of nanometal powder in propellant will probably be promising for its high reactive ability. The thrust of this work is to investigate the effect of nanometal powder on the decomposition characteristics of ammonium perchlorate (AP) which is the main oxidizer of composite solid rocket propellants. Understanding the complex physicochemical process that underlie the thermal decomposition of such AP can provide a link between the physical properties and molecular structure of these molecules and their combustive behavior, which in turn, may offer some clues for application of nanometal powder in propellant and explosive to obtain better control of their ignition, combustion or sensitivity.

## 2. Transition metals as catalyst

A catalyst is a compound that can affect the rate of a chemical reaction by providing an alternative and lower energy profile or pathway. It only has an effect on the rate of the reaction. That is, it only changes the cost of the activation energy. It is not related to the thermodynamics of the process and hence, the final product distribution. That is, if any process gives 90% product via a non-catalyzed pathway in 4 days, then a catalyst will help you get 90% product in say 4 h. So a catalyst affects the transition state and activation path. How does it do this? Typically, by complexing one of the reagents. Complexation by transition metals affords access to a wide variety of oxidation states for the metal. This has the property of providing electrons or withdrawing electrons from the transition state of the reaction. That is, if the transition state is electron rich, then the transition metal might hold some of that electron density and those prevent too much from building up on the reagent. This would then facilitate the reaction. Or the transition metal might undergo formal oxidation/reduction to achieve electron transfer to a substrate, thereby allowing a reaction to occur. This is "complexation and electron storage" taken to the extreme but is a common mechanism in organometallic chemistry. Indeed, a variety of catalytic pathways rely on a two electron transfer between the metal and the substrate (e.g. hydroformylation). It is the ability of the transition metal

to be in a variety of oxidation states, to undergo facile transitions between these oxidation states, to coordinate to a substrate, and to be a good source/sink for electrons that makes transition metals such good catalysts. Most industrially used catalysts are the transition metal in a bed, as a metal or bound structure. The above considerations are important but also the physical properties of absorption/adsorption and the electron band structure of the material.

### 3. Metal alloys

An alloy is a partial or complete solid solution of one or more elements in a metallic matrix. Complete solid solution alloys give single solid phase microstructure, while partial solutions give two or more phases that may be homogeneous in distribution depending on thermal (heat treatment) history. Alloys usually have different properties from those of the component elements.

Alloying one metal with other metal(s) or non metal(s) often enhances its properties. For example, steel is stronger than iron, its primary element. The physical properties, such as density, reactivity, Young's modulus, and electrical and thermal conductivity, of an alloy may not differ greatly from those of its elements, but engineering properties, such as tensile strength (Ball and Garwin, 1992) and shear strength may be substantially different from those of the constituent materials. This is sometimes due to the sizes of the atoms in the alloy, since larger atoms exert a compressive force on neighboring atoms, and smaller atoms exert a tensile force on their neighbors, helping the alloy resist deformation. Sometimes alloys may exhibit marked differences in behavior even when small amounts of one element occur. For example, impurities in semi-conducting ferromagnetic alloys lead to different properties, as first predicted by White, Hogan, Suhl, Tian Abrie and Nakamura (Ball and Garwin, 1992; Michael Hogan, 1969; Shufen et al., 2002). Some alloys are made by melting and mixing two or more metals. Bronze, an alloy of copper and tin, was the first alloy discovered, during the prehistoric period now known as the Bronze Age; it was harder than pure copper and originally used to make tools and weapons, but was later superseded by metals and alloys with better properties. In later times bronze has been used for ornaments, bells, statues, and bearings. Brass is an alloy made from copper and zinc.

Unlike pure metals, most alloys do not have a single melting point, but a melting range in which the material is a mixture of solid and liquid phases. The temperature at which melting begins is called the solidus, and the temperature when melting is just complete is called the liquidus. However, for most alloys there is a particular proportion of constituents (in rare cases two)—the eutectic mixture—which gives the alloy a unique melting point.

### 4. Ammonium perchlorate

Ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$  or AP) is the most widely used energetic material. It is an important oxidizer used in solid rocket propellants known as ammonium perchlorate composite propellants (APCP). Uses include the Space Shuttle Solid Rocket Boosters, manufactured by Alliant Techsystems (ATK), as well as many other solid rockets including some fireworks,

amateur and hobby high powered rockets, and larger rockets used for space launch and military purposes. Unfortunately, AP is also one of the least understood energetic materials. Over the past several decades numerous papers have been devoted to the decomposition mechanism and structural properties of AP. The decomposition of AP is rather complicated; mainly because this simple molecule consists of four different elements N, H, Cl, and O. If one considers all the potential oxidation states of these four elements, over 1000 possible chemical reactions can be written for the decomposition of AP (Brill et al., 2000). In addition, what makes AP completely different from other propellant and explosive ingredients is the presence of chlorine. Most, if not all, other energetic materials consist of only carbon, hydrogen, nitrogen, and oxygen. (Exceptions to this are the recently developed organic difluoramino structures.) Furthermore, impurities play a significant role in the decomposition, combustion, and burn rate of AP materials. Because of these complications the reaction Chemistry of AP is still largely not understood (Peiris et al., 2000). AP is the most common oxidizer in composite solid propellants (CSPs). Thermal decomposition characteristics of AP influence the combustion behaviour of the propellants (Singh et al., 2009a,b,c; Singh and Felix, 2003). AP based composite solid propellants require combustion modifiers to achieve higher burning rates and conventionally transition metal oxides (TMOs) are used as the burning rate modifiers (Carnes and Klabunde, 2003; Kishore and Sunitha, 1979a,b; Singh and Felix, 2003). Previous studies suggested that the burning rate modifiers are active mainly in the condensed phase and hence activity of the catalysts during condensed phase thermolysis of AP can be a good indicator to the catalytic activity of the additive during combustion of CSPs (Singh and Pandey, 2002).

#### 4.1. Synthesis

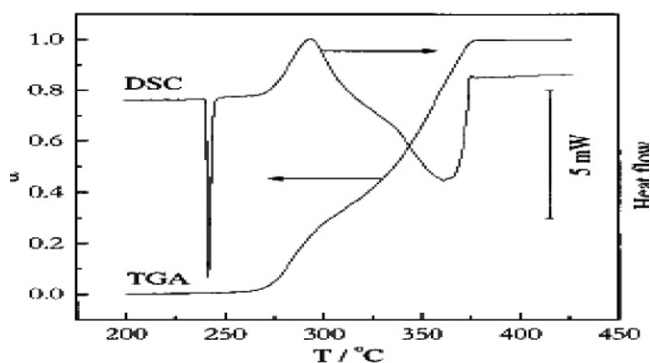
In literature several methods are reported for the synthesis of AP. Some of the most commonly used are mentioned here.

Dotson (1993) reported that Perchloric acid,  $\text{HClO}_4$ , and ammonium perchlorate,  $\text{NH}_4\text{ClO}_4$ , of high purity have been produced by electrolysis of chloric acid and subsequent reaction with high purity ammonium hydroxide to produce ammonium perchlorate. The process involves no alkali metals, chlorides or transition metals such as chromates, and thus produces propellant and explosive grade ammonium perchlorate of high purity and with no associated instability or pollution problems. The products can be recovered by solution crystallization-drying or direct spray-drying, respectively.

Vogt et al. (2002) reported that AP is produced by reaction between ammonia and perchloric acid, and is the driver behind the industrial production of perchloric acid. It also can be prepared by treatment of ammonium salts with sodium perchlorate. This process exploits the fact that the solubility of  $\text{NH}_4\text{ClO}_4$  is about 10% of that for sodium perchlorate

#### 4.2. Properties

AP is a white crystalline substance; it is used as the most common oxidizer in composite solid propellants (CSPs). The characteristic of the thermal decomposition of AP are believed to influence the performance of CSPs and are remarkably



**Figure 1** Combined plot of TGA and DSC experiments carried out at a heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  of AP.

sensitive to additives. The transition metal oxides are used as a burning rate modifier for CSPs (Ma et al., 2004; Said and Al-Qusami, 1996; Singh and Ojha, 2002; Wang et al., 2005; Zhu et al., 2002, 2004). Two most important crystal modifications of AP are: orthorhombic (region of existence:  $T < 240\text{ }^{\circ}\text{C}$ ) (Fig. 1) and cubic one, which is stable at temperatures  $T > 240\text{ }^{\circ}\text{C}$ . Heat of phase transition of AP from orthorhombic to cubic modification is  $11.3\text{ kJ/mol}$  (Evans et al., 1964). Investigation with the help of NMR, neutron diffraction (Ibers, 1960) and ESR (Dubovitsky et al., 1964) shows that both the ammonium and perchlorate ions can rotate freely. In the cubic structure, both ions rotate; in the orthorhombic one, only ammonium does.

It was assumed that the phase transition of the first type at  $240\text{ }^{\circ}\text{C}$  is preceded by the transition of the second type, which is the main reason of deviation from the normal behavior observed in ammonium perchlorate under thermal decomposition (Keenan and Siegmund, 1969)

Polymorphous transition in ammonium perchlorate crystals was studied in Ivanov and Boldyrev (1979). Several experimental results show that there are two mechanisms of the transformation of the rhombic modification into cubic one. At low-temperature, the transition follows atom-by-atom mechanism. As temperature increased up to  $243\text{ }^{\circ}\text{C}$ , the transition is of martensite type. In both cases, the polymorphous transition proceeds through the formation and growth of the nuclei of the new phase; the growth of martensite nuclei occurs not continuously but jump wise. The interface boundary can be coherent during the transition from rhombic modification into the cubic one (Ivanov and Boldyrev, 1979). During this process, the (0 1 1) plane of the rhombic modification corresponds to the (0 0 1) plane of the cubic one. One more curious fact was observed during investigation of thermal decomposition of ammonium perchlorate: the rate of thermal decomposition sharply decreases at the moment of phase transition (Jacobs and Ng, 1974; Pavlyuchenko et al., 1977) because rearrangement of the lattice from the rhombic into cubic at the moment of transition results in sharp worsening of the conditions for the accumulation of products catalyzing thermal decomposition in the system. In earlier works (Bircomshaw and Newman, 1955), this effect was explained by a decrease in the lattice parameters.

The experimental results show that at the behavior of ammonium perchlorate under the pressure up to 25 GPa at temperatures slightly above  $240\text{ }^{\circ}\text{C}$  (the point of transition

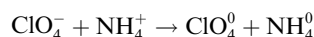
from the rhombic modification to the cubic one), melting is observed (Foltz and Meinschein, 1995).

#### 4.3. Mechanism of thermal decomposition

Several studies were carried out to understand the mechanism of decomposition of AP (Manelis, 1981; Solymosi, 1977). Reviews by Hall and Pearson, 1967; Jacobs and Whithead, 1969; Kishore and Sunitha, 1979a,b give good accounts of the mechanism of thermal decomposition of AP. Several mechanisms are proposed, but still it remains a matter of debate.

##### 4.3.1. Electron transfer mechanism

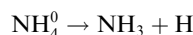
According to this mechanism (Jacobs and Russel-Jones, 1967a,b; Raevsky and Manelis, 1963), decomposition occurs due to electron transfer from anion to cation.



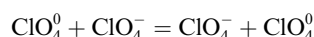
Probability of electron realization is higher because distance between the ions is smaller.

Because of this, an efficient acceptor of electrons is considered to be not any ammonium ion but only those located in interstices.

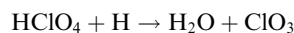
After accepting electron ammonium radical decomposed in to ammonia and hydrogen atom.



Hydrogen migrates over the lattice. Electron migrates exactly in the same manner over the anion sublattice:



As a result of the interaction between  $\text{ClO}_4$  radical and H,  $\text{HClO}_4$  is formed. It may continue interacting with H:



The  $\text{ClO}_3$  radical is a trap for electrons. Having trapped an electron, it is transformed into  $\text{ClO}_3^-$  ion. After that, chlorite ion and  $\text{ClO}_4$  radical can decompose; interact with  $\text{NH}_4^+$  ions, etc. As a result of interaction, secondary products are formed; among them, the major ones are chlorine, nitrogen hemi oxide and water.

Raevsky and Manelis (1963) have considered electron transition within the energy-band theory, that is, as the transition of an electron from the valence band into conduction band.

The AP is a typical dielectric; hence at low temperature of thermal decomposition, the process cannot be sustained by electron transfer because of its low probability, this rules out the possibility of electron transfer mechanism. The primary products detected in the experiments by different researchers were ammonia and perchloric acid. This allowed assuming that the primary stage of process of thermal decomposition of AP is proton transfer.

##### 4.3.2. Proton transfer mechanism

Similar value of activation energies of thermal decomposition and sublimation (Jacobs and Russel-Jones, 1967a,b), identical composition of the products of decomposition (Svetlov and Koroban, 1967) and sublimation (Svetlov and Koroban, 1970), inhibition of the reaction in ammonia vapour (Boldyrev et al., 1970) and acceleration in the vapour of perchloric acid



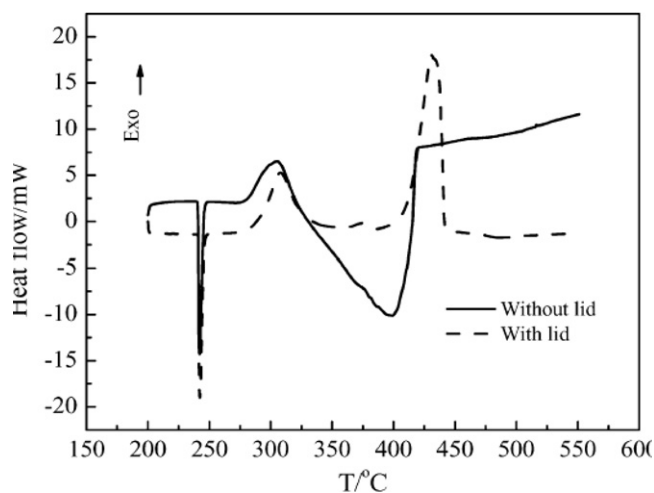
(Jacobs and Russel-Jones, 1967a,b; Savintsev et al., 1972), favor protons transfer mechanism. A scheme of thermal decomposition of ammonium perchlorate proposed by Jackobs can be presented as a version of proton mechanism (Boldyrev, 2006; Jacobs and Russel-Jones, 1967a,b):



Step I involves pair of ions in perchlorate ammonium lattice. Step II involves the decomposition step that starts with proton transfer from the cation  $\text{NH}_4^+$  to the anion  $\text{ClO}_4^-$  via molecular complex and which then in Step III decomposes into ammonia and perchloric acid (Figs. 1 and 2). The molecules of  $\text{NH}_3$  and  $\text{HClO}_4$  either react in the adsorbed layer on the surface of perchlorate or desorb and sublime interacting in the gas phase. Many reactions occur rapidly in the gas phase between  $\text{NH}_3$  and  $\text{HClO}_4$ , forming the side products such as  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{Cl}_2$ ,  $\text{NO}$ , and  $\text{H}_2\text{O}$  at low temperature ( $< 350^\circ\text{C}$ ). An essential feature of the process of thermal decomposition of ammonium perchlorate is that the process occurs not at the very surface but in pores beneath it at a distance of about several microns. This is a difference of thermal decomposition of ammonium perchlorate from its sublimation.

During a process occurring in the adsorbed layer it was assumed and reported in earlier reports (Jacobs and Russel-Jones, 1967a,b) that perchloric acid is desorbed more rapidly than ammonia, which causes incomplete oxidation of ammonia, creating a saturated atmosphere (Jacobs and Russel-Jones, 1967a,b) of  $\text{NH}_3$ . As a result, high-temperature decomposition decelerates and undergoes incomplete transformation. During the second exothermic decomposition  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{H}_2\text{O}$  products were formed in the gas phase reactions.

The process of thermal decomposition both at low and high temperatures has a common start, which is proton transfer from the cation  $\text{NH}_4^+$  to the anion  $\text{ClO}_4^-$ . The difference between the decomposition of low-temperature orthorhombic modification and the high-temperature cubic one arises when the secondary processes occur. These processes during the decomposition of orthorhombic and cubic modifications differ both in the character of chemical processes and in the topography of their course. The decomposition of the low-temperature



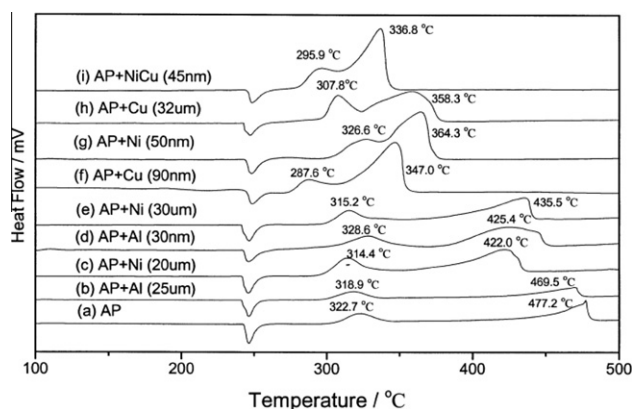
**Figure 2** DSC thermogram: comparisons between AP in an open sample holder and in a sample holder with a pierced lid at  $12^\circ\text{C min}^{-1}$ .

orthorhombic modification proceeds in the pores beneath the surface in the sites where the secondary products of dissociation can be accumulated, and in the sites where the conditions for regeneration of active centers exist, either due to pressure of the gases formed in a pore or due to decomposition of perchloric acid and interaction of the products of its decomposition with ammonia. It is the condition for secondary processes, providing the feedback between the accumulation of reaction products and the formation of new active centers that act as the main reasons of decomposition of the orthorhombic modification. Because of this, the action of additives, irradiation and other factors affecting the reactivity of the initial crystal is mainly restricted to the initial period of reaction, its initiation. The situation changes when higher temperature is employed, and when we come across decomposition of the cubic modification. In this case, the major role is played by the processes taking place on the surface of the crystal: adsorption and desorption of ammonia and chloric acid; so, the role of the primary processes connected with proton transfer increases. A result larger is the effect of the introduction of dopants, which change the concentration of protons in the lattice during the decomposition of the cubic modification, and stronger effect of ammonia. The hypothesis formulated by Kaidymov and Gavazova (1974a,b) is likely to be worth mentioning; it says that the catalytic activity of the orthorhombic modification with respect to the decomposition of perchloric acid, an important stage through which thermal decomposition proceeds, is much higher than that of the cubic modification. So, in spite of advances in investigating the mechanism of thermal decomposition of ammonium perchlorate, mechanism is still unclear.

#### 4.4. Solid rocket propellants

Solid propellant motors are the simplest of all rocket designs. They consist of a casing, usually steel, filled with a mixture of solid compounds (fuel and oxidizer) which burn at a rapid rate, expelling hot gases from a nozzle to produce thrust. When ignited, a solid propellant burns from the center out towards the sides of the casing. The shape of the center channel determines the rate and pattern of the burn, thus providing a means to control thrust. Unlike liquid propellant engines, solid propellant motors can not be shut down. Once ignited, they will burn until all the propellant is exhausted. There are two families of solids propellants: homogeneous and composite. Both types are dense, stable at ordinary temperatures, and easily storable. Homogeneous propellants are either simple base or double base. A simple base propellant consists of a single compound, usually nitrocellulose, which has both an oxidation capacity and a reduction capacity. Double base propellants usually consist of nitrocellulose and nitroglycerine, to which a plasticiser is added. Homogeneous propellants do not usually have specific impulses greater than about 210 seconds under normal conditions. Their main asset is that they do not produce traceable fumes and are, therefore, commonly used in tactical weapons. They are also often used to perform subsidiary functions such as jettisoning spent parts or separating one stage from another.

Modern composite propellants are heterogeneous powders (mixtures) which use a crystallized or finely ground mineral salt as an oxidizer, often ammonium perchlorate, which constitutes between 60% and 90% of the mass of the propellant. The



**Figure 3** DTA curves for decomposition of AP and as catalyzed by metal powders (5 wt%).

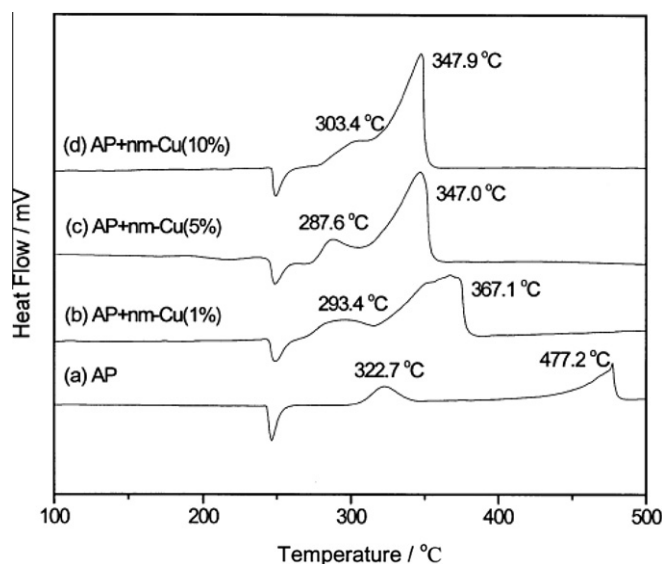
fuel itself is generally aluminum. The propellant is held together by a polymeric binder, usually polyurethane or polybutadiene, which is also consumed as fuel. Additional compounds are sometimes included, such as a catalyst to help increase the burning rate, or other agents to make the powder easier to manufacture. The final product is rubber like substance with the consistency of a hard rubber eraser.

Composite propellants, as the name implies are mixtures of an oxidizer, usually an inorganic salt such as ammonium perchlorate in a hydrocarbon fuel matrix, such as asphalt like material. Usually composite propellants are cast to shape so that the rocket fuel is added with small particles of oxidizers that are dispersed throughout. The fuel is called a binder because the oxidizer has no mechanical strength. In both cases fuel and oxidizer are mixed and undergo combustion only on surface, they are placed directly into combustion chamber. Rocket fuel burns until it gets exhausted, which involves changing the effective size and shape during the operation. As it burns only on surface, shape and area of propellant are regulated. Solid rocket fuels burn rapidly by expelling hot gases from nozzle to produce thrust depending on the mass flow rate which in turn depends on the solid rocket fuel

consumed per second. The only problem is once ignited the motor can not be shut down until the fuel is exhausted. Composite propellants are often identified by the type of polymeric binder used. The two most common binders are polybutadiene acrylic acid acrylonitrile (PBAN) and hydroxy-terminator polybutadiene (HTPB). PBAN formulations give a slightly higher specific impulse, density, and burn rate than equivalent formulations using HTPB. However, PBAN propellant is the more difficult to mix and process and requires an elevated curing temperature. HTPB binder is stronger and more flexible than PBAN binder. Both PBAN and HTPB formulations result in propellants that deliver excellent performance, have good mechanical properties, and offer potentially long burn times. Solid propellant motors have a variety of uses. Small solids often power the final stage of a launch vehicle, or attach to payloads to boost them to higher orbits. Medium solids such as the Payload Assist Module (PAM) and the Inertial Upper Stage (IUS) provide the added boost to place satellites into geosynchronous orbit or on planetary trajectories. The Titan, Delta, and Space Shuttle launch vehicles use strap-on solid propellant rockets to provide added thrust at liftoff. The Space Shuttle uses the largest solid rocket motors ever built and flown. Each booster contains 500,000 kg (1,100,000 pounds) of propellant and can produce up to 14,680,000 Newtons (3,300,000 pounds) of thrust.

### 5. Effect of metal and alloys on thermal decomposition of AP

Nanometer sized catalysts are expected to possess better catalytic property as compared to their bulk size. It is generally observed that since catalytic activity is primarily a surface phenomenon, size reduction of the catalyst increases the surface area and hence the catalytic activity is also increased. Activities of the solid catalysts increase many fold by size reduction in to the nanometer scale (Jacobs and Kureishy, 1962; Singh et al., 2008, 2009a,b,c). There is considerable current interest in the decomposition behavior of ammonium perchlorate (AP) since it is widely used as an oxidizer in burning process. Thermal decomposition characteristics of AP influence the combustion behavior of the propellants. AP based



**Figure 4** DTA curves for decomposition of AP as catalyzed by nanometer Cu powder with different content.

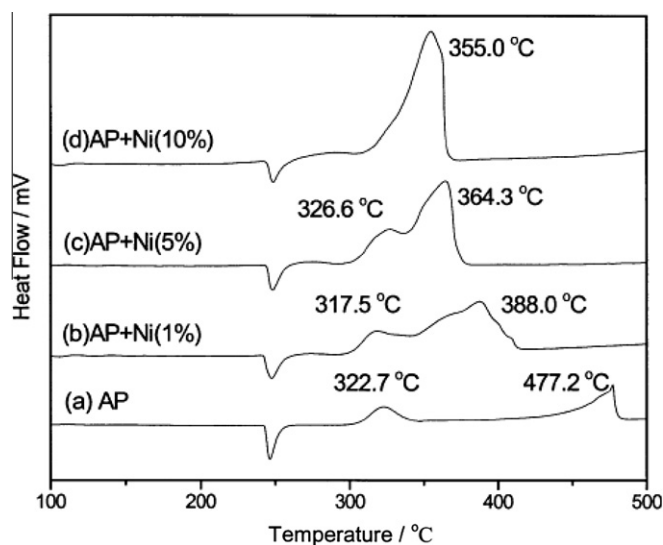


Figure 5 DTA curves for decomposition of AP as catalyzed by nanometer Ni powder with different content.

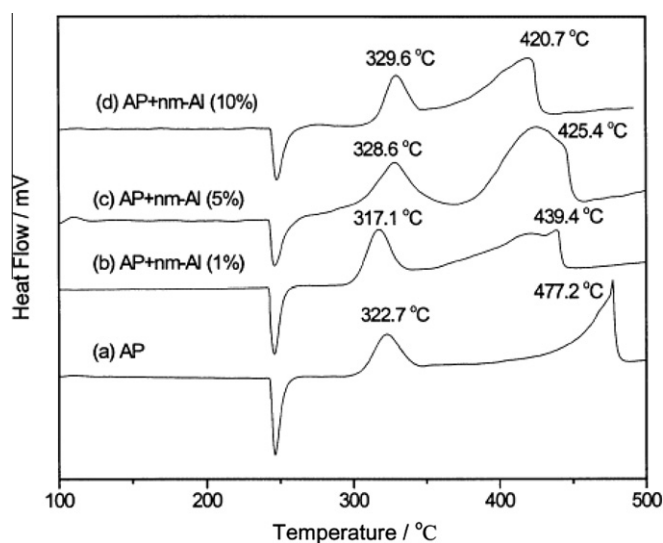


Figure 6 DTA curves for decomposition of AP as catalyzed by nanometer Al powder with different content.

**Table 1** The DTA peak temperature ( $t_{\max}$ ), heat released ( $H$ ) and active energy ( $E$ ) (Liu et al., 2004b).

| Sample          | $t_{\max}$ (°C) |             | $\Delta H$ (kJ g <sup>-1</sup> ) | $E$ (kJ mol <sup>-1</sup> ) |             |
|-----------------|-----------------|-------------|----------------------------------|-----------------------------|-------------|
|                 | First step      | Second step |                                  | First step                  | Second step |
| AP              | 322.7           | 477.2       | 0.436                            | 100                         | 177         |
| AP/Cu (90 nm)   | 287.6           | 347         | 1.20                             | 93                          | 155         |
| AP/Ni (50 nm)   | 326.6           | 364.3       | 1.32                             | 111                         | 167         |
| AP/Al (30 nm)   | 328.6           | 425.4       | 0.903                            | 121                         | 172         |
| AP/NiCu (45 nm) | 296.5           | 336.8       | 1.2                              | 106                         | 154         |
| AP/Cu (26 nm)   | 307.8           | 358.3       | 1.09                             |                             |             |
| AP/Ni (20 nm)   | 314.4           | 422.0       | 0.727                            |                             |             |
| AP/Ni (30 nm)   | 315.2           | 435.5       | 0.58                             |                             |             |
| AP/Al (25 nm)   | 318.9           | 469.5       | 0.302                            |                             |             |

composite solid propellants (CSPs) require combustion modifiers to achieve higher burning rates and conventionally

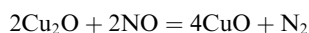
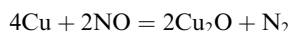
transition metal oxides are used as the burning rate modifiers. Previous studies suggested that the burning rate modifiers are

active mainly in the condensed phase and hence activity of the catalysts during condensed phase thermolysis of AP can be a good indicator to the catalytic activity of the additive during combustion of CSPs. All experiments are done under atmospheric condition.

Liu et al. (2004a,b) investigated the effect of metal nanopowder on thermal decomposition of AP and comparative investigation also done on their micron size particle. Their result revealed that the decomposition of AP in the presence of nanometer metal powders show a noticeable change in the decomposition pattern (Fig. 3). The endothermic peak shows no changes in position. In contrast, there are big differences in the second exothermic peak. Their position depends strongly on the nanometer metal powders. The additions of nanometer Cu, Ni and Al powders lower the high decomposition temperature of AP by 130.2 °C, 112.9 °C and 51.8 °C respectively. This indicates that nanometer Cu, Ni and Al powders have an obvious catalytic effect on the main exothermic decomposition of AP (Fig. 4–6). Of the three, nanometer Cu shows the best catalysis for promoting the decomposition of AP, followed by nanometer Ni which also has good catalytic effect and nanometer Al. On the other hand, the addition of nanometer Cu decreased the first exothermic decomposition temperature by 35.1 °C, while nanometer Ni and Al powders increased that by 3.9 °C and 5.9 °C respectively. Only nanometer Cu powder shows marked catalytic effect both on low temperature decomposition of AP, while nanometer Ni and Al powders hinder it. In addition, the total DTA heat releases of AP in the presence of nanometer Ni, Cu and Al were 1.32 kJ/g, 1.20 kJ/g and 0.903 kJ/g, respectively. These are much larger than that of pure AP, indicating that the decomposition of AP was enhanced (Table 1).

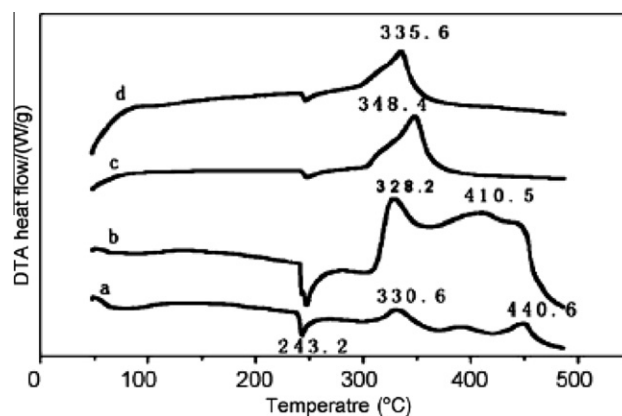
From Fig. 3, it can be seen that the second exothermic decomposition temperature of AP is decreased by 140.4 °C in the presence of NiCu powder, and the decrease is more significant than that which occurs with nanometer Ni or Cu powder. It is obvious that nanometer NiCu powder has higher catalytic activity in the decomposition of AP than that of nanometer Ni or Cu powder. Mechanism of thermal decomposition of AP was suggested by proton transfer mechanism.

As reported earlier Cu nanopowder contains many defects over crystal lattice. Atoms on the defects are not saturated and tend to become steady by absorbing materials with surplus electrons onto its surface. The N atom of AP contains surplus electrons, so the N–X bond becomes weak and easy to break owing to the absorbing of the N atom on the surface of Cu atom. This is advantageous in the production of NH<sub>3</sub>. It is also reported (Zhi and Feng-Qi, 2002) that nitrogen oxides react easily with Cu:



Because the nitrogen oxides are produced both at the first and second decomposition step of AP, the nanometer Cu can accelerate the decomposition of AP by catalyzing the decomposition of nitrogen oxides. Because of both these effects, nanometer Cu powder shows high catalytic effect on the first and second decomposition step of AP.

Nanometer Cu, Ni, Al and NiCu powders decreased the active energy of the high temperature decomposition of AP by



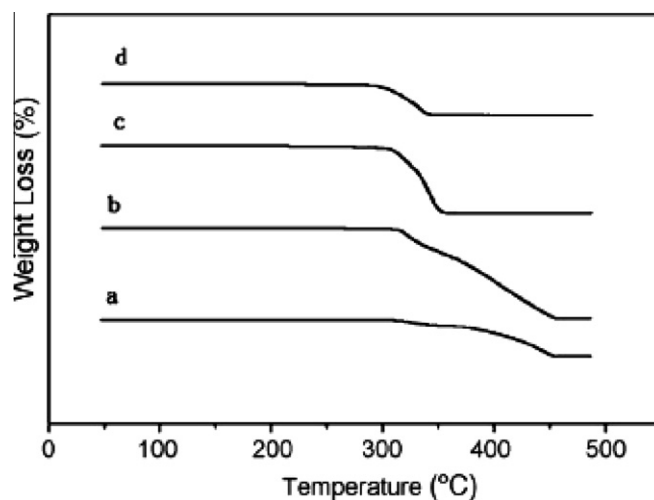
**Figure 7** DTA curves of samples of AP with different Ni particles: (a) pure AP, (b) AP+micrometric Ni (2 wt.%), (c) AP+Ni (2 wt.%) and (d) AP+Ni (5 wt.%).

22 kJ/mol, 10 kJ/mol, 5 kJ/mol and 23 kJ/mol respectively, indicating that they can easily facilitate the thermal decomposition of AP at high temperature. Nanometer Cu and NiCu powders also decreased the active energy of AP at low temperature decomposition, while nanometer Ni and Al powders increased it. The DTA curves of AP in the presence of metal micron-sized powders were shown in Fig. 3. It can be seen that metal micron-sized powders can decrease the second decomposition temperature, showing good catalytic activity, but their effects are obviously less than those of nanopowders. In the mixture of AP and nanometer metal powders, nanometer metal powders maybe mostly absorbed on the surface of AP particles due to their small average size and huge surface area, and most of AP surface can be covered by nanometer metal powders with enough content.

The increase in the content of nanometer powders would enhance this effect. This may be due to more efficient heat transfer by metal particles in the mixture. Therefore, the results are that the first decomposition temperature of AP generally increases as the content of nanometer metal powders increase. In a comparison with nanometer metal powders, micrometer metal powders cover much less surface of AP particles and therefore do not produce a clear hindering effect. So with the same content of metal powders, micrometer metal powders slightly lower the first decomposition peak of AP while nanometer metal powders increase it.

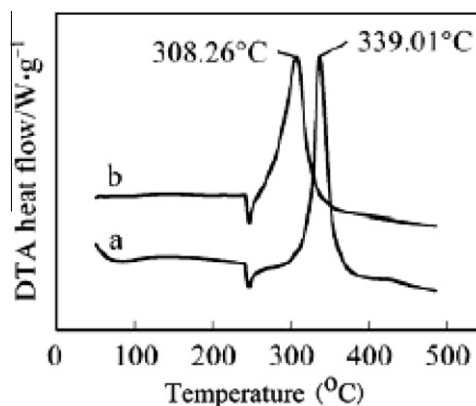
Duan et al. (2008a,b) reported that Ni nanoparticles have significant catalytic effect on the decomposition of ammonium perchlorate (AP). Compared with the thermal decomposition of pure AP, adding Ni nanoparticles (2–5 wt.%) in AP decreases its decomposition temperature by 92–105 °C and increases its apparent decomposition heat by 787.1–796.1 J/g, investigated by DTA and TG. Such effect is attributed to the large specific surface area and the active chemical nature of Ni nanoparticles. These results are useful for the controlled synthesis of Ni nanoparticles in good quality to be used in the AP-based propellant. The same peak at 243.2 °C appeared in all samples containing Ni particles, indicating that the Ni species has little effect on the crystallographic transition temperature of AP (Fig. 7). However, dramatic changes in the exothermic peak of AP decomposition have been observed in



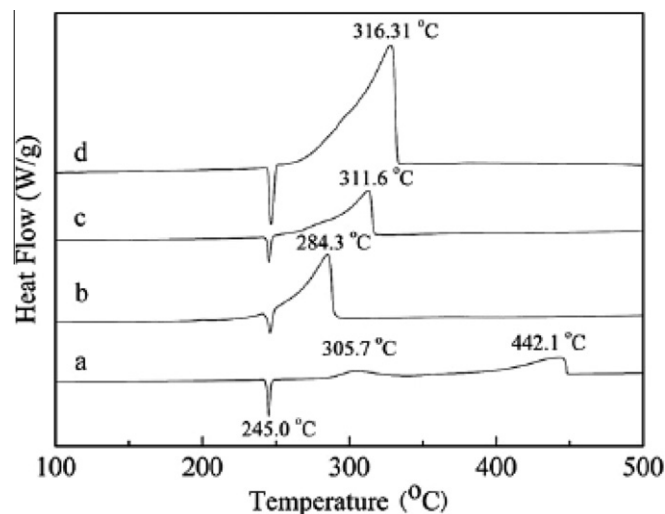


**Figure 8** TG pattern of samples of AP with different Ni particles: (a) pure AP, (b) AP + micrometric Ni (2 wt.%), (c) AP + Ni (2 wt.%) and (d) AP + Ni (5 wt.%).

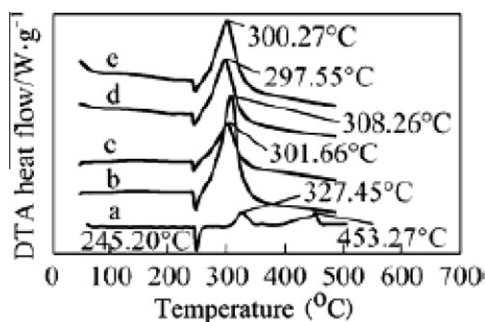
relatively high temperature region after adding Ni particles. When the micrometric Ni powders was added to the AP, the first exothermic peak shifted from 330.6 to 328.2 °C, and the second exothermic peak shifted significantly from 440.6 to 410.0 °C (Fig. 7b). However, after adding the Ni nanoparticles (Fig. 7c and d), the two exothermic peaks of AP only one peak centered was obtained at 335–348 °C. The original large exothermic peak at 440 °C for pure AP disappeared. These results indicate the significant effect of Ni nanoparticles on the decrease of the decomposition temperature of AP. In addition, the relatively high content of Ni favors the further decreasing of the decomposition temperature of AP. Comparing the size and content of Ni particles has a deep understanding of the effect of Ni nanoparticles on decomposition of AP. It is clear that the effect of Ni nanoparticles with average size of 36 nm (2% in AP) is more than that of micrometric Ni particles (2% in AP) and the Ni nanoparticles with average size of 50 nm (5% in AP) in previous results (Tan et al., 2004), which decreases the decomposition temperature of AP by 92, 30,



**Figure 10** DTA curves for (a) AP +  $\mu\text{m-Co}$  (2%) and (b) AP + nm-Co (2%).



**Figure 9** DSC curves for the decomposition of the AP catalyzed by different morphologic cobalt catalyst: (a) pure AP, (b) AP + snowflake-like Co, (c) AP + cauliflower-like Co and (d) AP + ball-like Co.

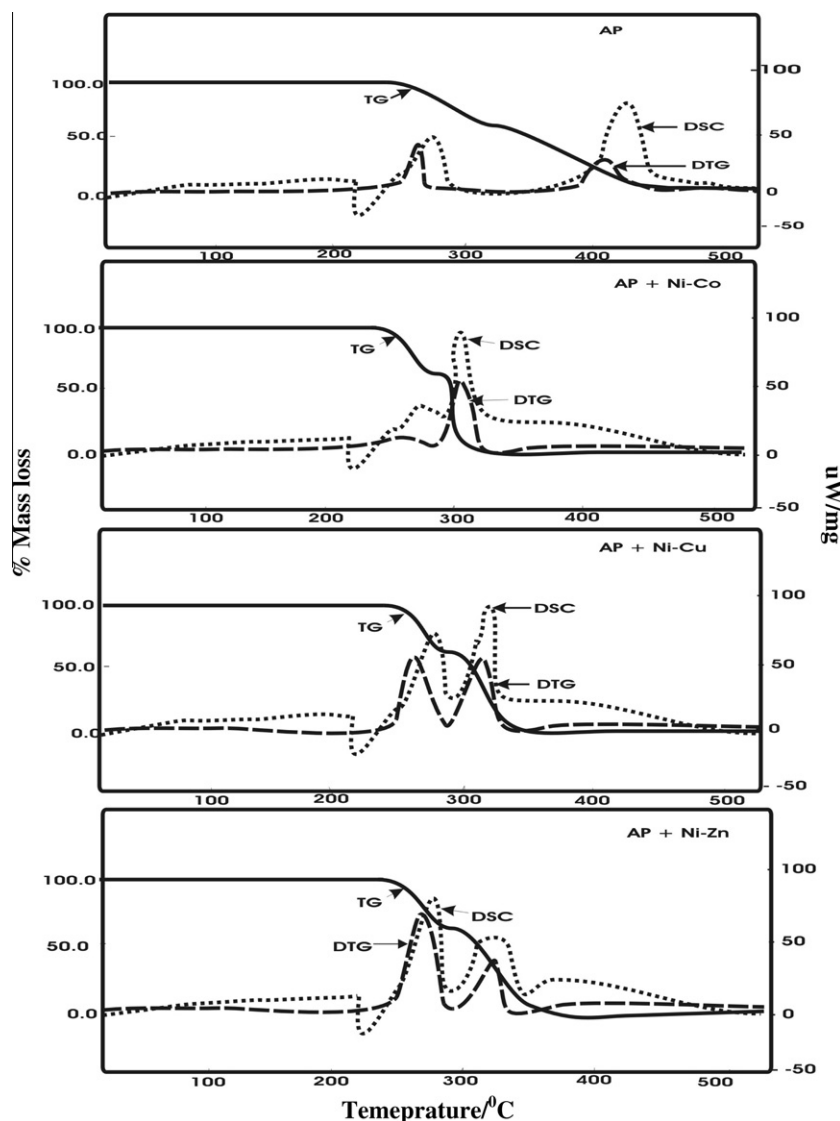


**Figure 11** DTA curves for pure AP and the mixtures of Co and AP.

76 °C, respectively (Fig. 8). The results are reasonable as considering the large specific surface area of small nanoparticles and their potential high surface energy producing high activity. However, the comparison of the effect of Ni nanoparticles (36 nm, 2% in AP) and that of NiO nanoparticles (10 nm,

~3% in AP) in previous work (Wang et al., 2005) suggests the much complex effect of Ni nanoparticles. The Ni nanoparticles (36 nm, 2% in AP) and the NiO nanoparticles (10 nm, ~3% in AP) decrease the thermal decomposition of AP by 92 and 93 °C, respectively. Since the ratio of atoms in the outer surface to its total atoms for a particle with diameter of 10 nm is about 4–5 times than that with diameter of 36 nm, the above nearly same decreasing temperature effect of Ni nanoparticles with low loading in AP and large size as NiO nanoparticles with higher loading and small size suggests the significantly higher activity of Ni nanoparticles than NiO nanoparticles.

The effects of aluminum (Al) and nickel (Ni) powders of various grain sizes on the thermal decomposition of ammonium perchlorate (AP) were investigated (Zhi et al., 2006) by TG and DSC in a dynamic nitrogen atmosphere. The TG results show that Al powders have no effect on the thermal decomposition of AP at conventional grain size, while the nanometer-sized Ni powders (n-Ni) have a great influence on the thermal decomposition of AP with conventional and superfine grain size. The results confirmed the promoting effects of n-Ni. The effects of n-Ni have been ascribed to its



**Figure 12** TG-DTG-DSC thermogram.

**Table 2** DTG and DSC phenomenological data of the AP and AP with nanoalloys (Singh et al., 2009a).

| Samples           | DTG             |        | DSC             |        |
|-------------------|-----------------|--------|-----------------|--------|
|                   | Peak (temp./°C) | Nature | Peak (temp./°C) | Nature |
| AP                | 282             | Exo    | 285             | Exo    |
|                   | 410             | Exo    | 420             | Exo    |
| AP + Ni-Co (1%wt) | 267             | Exo    | 275             | Exo    |
|                   | 300             | Exo    | 300             | Exo    |
| AP + Ni-Cu (1%wt) | 277             | Exo    | 279             | Exo    |
|                   | 324             | Exo    | 325             | Exo    |
| AP + Ni-Zn (1%wt) | 290             | Exo    | 280             | Exo    |
|                   | 340             | Exo    | 336             | Exo    |

enhancement on the gas phase reactions during the second step decomposition of conventional grain size AP.

As reported (Ping et al., 2006) In the presence of Cu/CNT composite particles, the peak temperature of the high-temperature decomposition of ammonium perchlorate (AP) decreased by 126.3 °C, and the peak of the low-temperature decomposition disappeared. Compared with a sample of simply mixed Cu and CNTs, the peak temperature of the high-temperature decomposition of AP-Cu/CNTs composite particles is decreased by 11.4 °C. Compared with Cu, the peak temperature of the high-temperature decomposition of AP-Cu/CNT composite particles is decreased by 20.9 °C. This work shows that the catalytic performance of Cu on the thermal decomposition of AP can be improved by compounding with CNTs.

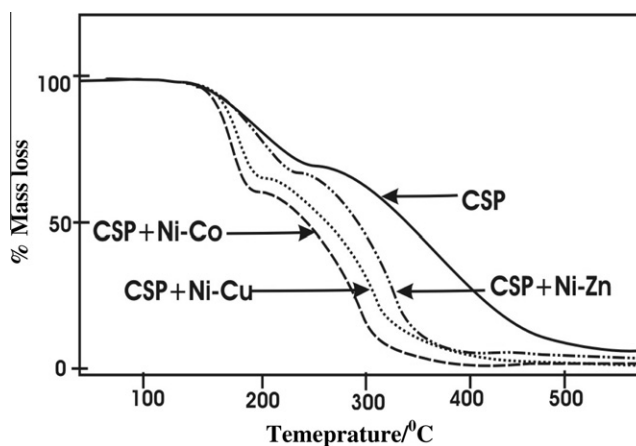
The effect of metal nanopowders (Al, Fe, W, Ni, Cu, and Cu-Ni alloys) on the decomposition of AP with DTA-TGA method was studied (Gromov et al., 2009) and it was found that the catalytic action appears in the case of Cu-Ni nanopowders. The temperature of decomposition of energetic materials with the addition of metal nanopowders could be lowered by 161 °C for AP.

According to DSC patterns for the decomposition of AP at both low and high temperatures were significantly changed with the addition of cobalt nanocrystals (Liu et al., 2009). Irrespective of the shapes of the added cobalt, the two decomposition peaks of the pure AP were immersed into one peak for the composites. Moreover, the starting temperature for the decomposition of the composites was obviously lower than that for the decomposition of the pure AP. Based on the morphologies of the cobalt added, the maximum peak temperature for the decomposition of the composites followed the decreasing order of ball-like (316.3°C), cauliflower-like (311.6 °C), and snowflake-like (284.3 °C) cobalt. These observations clearly indicate that the cobalt nanocrystals were efficient to promote the decomposition of the AP, and the snowflake-like cobalt

**Table 4** Burning rate of CSPs with and without nanoalloys (1% by wt.) (Singh et al., 2009a).

| Sample              | Burning rate (mm/s) | $r^*/r$ |
|---------------------|---------------------|---------|
| CSP                 | 1.22                | 1.00    |
| CSP + Ni-Co (1% wt) | 2.08                | 1.71    |
| CSP + Ni-Cu (1%wt)  | 1.77                | 1.45    |
| CSP + Ni-Zn (1%wt)  | 1.59                | 1.30    |

$r^*$  and  $r$  is burning rate of CSP with and without nanoalloys respectively.

**Figure 13** TG thermogram of CSPs with and without Nanoalloys.

showed the highest performance in the aspect of decreasing the decomposition temperature. The BET surface areas of the cauliflower-like and snowflake-like cobalt nanocrystals

**Table 3** Ignition delay ( $D_i$ ), activation energy for ignition delay ( $E_a$ ) and correlation coefficient of AP and AP + nanoalloys (1% by wt.) (Singh et al., 2009a).

| Sample            | $D_i$ (s)      |                |                |                |                | $E_a$ (kJ/mol) | $r$ (correlation coefficient) | $-\ln A$ |
|-------------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------------------------|----------|
|                   | $360 \pm 1$ °C | $375 \pm 1$ °C | $390 \pm 1$ °C | $405 \pm 1$ °C | $420 \pm 1$ °C |                |                               |          |
| AP                | 105            | 93             | 85             | 71             | 60             | 49.14          | 0.9897                        | 4.65     |
| AP + Ni-Co (1%wt) | 64             | 59             | 53             | 48             | 45             | 22.18          | 0.9977                        | 0.04     |
| AP + Ni-Cu (1%wt) | 75             | 68             | 64             | 55             | 48             | 26.78          | 0.9849                        | 0.75     |
| AP + Ni-Zn (1%wt) | 90             | 85             | 75             | 63             | 55             | 31.13          | 0.9834                        | 1.37     |

**Table 5** Ignition delay ( $D_i$ ), activation energy for ignition delay ( $E_a$ ) and correlation coefficient of CSPs with and without nanoalloys (1% by wt.) (Singh et al., 2009a).

| Sample             | $D_i$ (s)                 |                           |                           |                           |                           | $E_a$ (kJ/mol) | $r$ (correlation coefficient) | $-\ln A$ |
|--------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|----------------|-------------------------------|----------|
|                    | $360 \pm 1^\circ\text{C}$ | $375 \pm 1^\circ\text{C}$ | $390 \pm 1^\circ\text{C}$ | $405 \pm 1^\circ\text{C}$ | $420 \pm 1^\circ\text{C}$ |                |                               |          |
| CSP                | 68                        | 62                        | 55                        | 52                        | 49                        | 20.3           | 0.9800                        | 0.36     |
| CSP + Ni-Co (1%wt) | 54                        | 50                        | 46                        | 44                        | 41                        | 16.5           | 0.9970                        | 0.67     |
| CSP + Ni-Cu(1%wt)  | 57                        | 53                        | 48                        | 45                        | 43                        | 17.7           | 0.9843                        | 0.85     |
| CSP + Ni-Zn (1%wt) | 62                        | 56                        | 50                        | 48                        | 46                        | 18.4           | 0.9800                        | 0.62     |

were measured to be of  $7.23$  and  $1.65\text{ m}^2\text{ g}^{-1}$ , respectively. This indicates that the catalytic ability of the cobalt for decreasing the decomposition of AP is not proportional to its surface area. Thus, the high catalytic performance of cobalt nanocrystals may be explained as that a great deal of cobalt lattice defects were formed during the liquid-phase reduction. Based on the DSC curves in Fig. 9, the apparent decomposition heat of the pure AP was calculated to be of  $0.437\text{ kJ g}^{-1}$ . When Co catalyst was added, the apparent decomposition heat increased to  $0.884$ ,  $1.040$ , and  $1.884\text{ kJ g}^{-1}$  for snowflake-like, cauliflower-like, and ball like Co, respectively.

Duan et al. (2008a,b) also reported similar results and comparison of our results of using Co nanoparticles (42 nm, 2% in AP) and those using  $\text{Co}_3\text{O}_4$  nanoparticles (35 nm, ~2% in AP) (Chen et al., 2005) suggests the much complex effect of Co. The former Co nanoparticles (42 nm, 2% in AP) and the latter  $\text{Co}_3\text{O}_4$  nanoparticles (35 nm, ~2% in AP) decrease the thermal decomposition of AP by  $145.01^\circ\text{C}$  and  $106.27^\circ\text{C}$ , respectively (Figs. 10 and 11). From the previous results, it is known that, in the first exothermic decomposition step of AP, a solid decomposition reaction occurs to produce large amount of  $\text{N}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$  and a small amount of  $\text{NO}$  (Foltz and Meinschein, 1995; Kaidymov and Gavazova, 1974a,b). The second exothermic decomposition step of AP is a gas phase reaction to produce large amount of  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{Cl}_2$  and  $\text{H}_2\text{O}$  etc. (Jacobs and Pearson, 1969; Rosser et al., 1968). In many catalytic processes, it is proved that oxygen species is preferably absorbed by the metallic species, as compared with  $\text{CO}$ ,  $\text{H}_2\text{O}$  etc., resulting in the following rapid reaction to form  $\text{CoO}$ . It is also normally observed that the metallic nanoparticle is apt to burn or explode quickly as exposed to air. In one word, metallic Co species is much unstable and active as compared with  $\text{CoO}$  species. Notably, the interaction of metallic Co species with  $\text{O}_2$  and  $\text{Cl}_2$  to form  $\text{CoO}$  and  $\text{CoCl}_2$  releases large amount of heat to be  $237.9\text{ kJ/mol}^{-1}$  and  $313\text{ kJ/mol}^{-1}$ , respectively. These rapid exothermic reactions may accelerate the decomposition of AP during the first stage. And when  $\text{CoO}$  is formed, the following catalytic reaction may be the same and still release large amount of heat (Liu et al., 2004a,b). Following the above mechanism, apparently, the enhancement effect of cobalt nanoparticles depends on its content to provide the reaction heat, well in consistency with our results as adding 2–7% (by mass) cobalt nanoparticles in the AP.

The catalytic effect of Zn nanopowders on thermal decomposition of ammonium perchlorate (AP) as well as those of Zn micropowders has been investigated (Song et al., 2008a,b) using differential thermal analysis (DTA). The results show that both nanometer and micrometer Zn powders show similar excellent catalytic effect on the decomposition of AP, while the

total heat releases of AP added by Zn nanopowders are generally higher than those of AP added by Zn micropowders.

Effect of Mg metal nanopowder on thermal decomposition of AP investigated (Song et al., 2008a,b) result revealed that the addition of a small amount of magnesium nanoparticles remarkably catalyzes the decomposition process of ammonium perchlorate by lowering the decomposition temperature and enhancing its heat output.

Singh et al. (2009c) investigated catalytic effect of Ni-Co, Ni-Cu, Ni-Zn on decomposition of AP and composite solid propellants (CSPs). TG thermogram (Fig 12) for AP with nanoalloys does confirm that nanocrystals affect both low temperature decomposition (LTD) and high temperature decomposition (HTD) of AP, addition of catalyst, not only increases the mass loss of AP but also lowers the HTD range of AP to form gaseous products. DTG, DSC also confirms lowering temperature of HTD (Table 2). Computational calculation shows that activation energy for ignition for AP is lowered by the nanoalloys (Table 3). Results reported in Table 3 clearly shows that nanoalloys enhanced the burning rate ' $r$ ' of CSPs which as highest for Ni-Co near about two times and lowest for Ni-Zn nanoalloy (Table 4). Most of the studies suggested that ballistic modifiers are active mainly in the condensed phase at AP-binder interface (Chakravarthy et al., 1997). TG thermograms shown in Fig 10 indicate that the condensed phase reactions are occurring in CSPs. CSPs have two step decomposition namely LTD and HTD whereas in case of propellants with nanoalloys, the thermal decomposition occurs at much lower temperature in case of HTD, which may be due to the activity of nanoalloys (Fig. 13). Ignition delay and their kinetic parameters are shown in Table 5. CSPs are also ignited with noise and flame at sudden high temperature. Computational calculation shows that activation energy for ignition of CSPs lowered by the nanoalloys. Summarizing these results, it may be inferred that nanoalloy can be used as catalyst for AP and CSPs.

The Ag-Ni bi-metal nanocrystals showed great potential as the additive in promoting the decomposition of ammonium perchlorate (AP) (Tang et al., 2009). To improve the catalytic activity of amorphous Co-B alloys, Co-B coated aluminum (Co-B/Al) nanocomposites were prepared by electrodeless coating technique and evaluated as additives for the catalytic performance of ammonium perchlorate (AP) and AP-based solid state propellants (Cheng et al., 2010). X-ray diffractometry (XRD), scanning electron microscopy (SEM), inductive coupled plasma emission spectrometry (ICP), differential scanning calorimetry (DSC) as well as strand burner method were employed to characterize the crystal phase, morphologies, chemical composition, and catalytic activity of the as-synthesized material. The results show that a continuous layer of



about 100 nm amorphous  $\text{Co}_{72.6}\text{B}_{27.4}$  covers the surfaces of Al particles. Addition of the as-synthesized Co-B/Al nanocomposites as catalysts promotes AP decomposition, enhances the burning rate, and lowers the pressure exponent of the AP-based propellants considerably.

## 6. Conclusion

Despite much research work on the effect of catalysts on the thermal decomposition of AP and combustion of composite systems based on AP; opinion is still differing with regard to the mechanism of the process. Studies of the thermal decomposition of ammonium perchlorate are interesting not only because of the application of the ammonium perchlorate as a component of solid propellant but the reaction provides a unique example of the auto-localization of thermal decomposition of a solid, when no solid products are formed, and the feed-back during the reaction is due to the secondary reactions, in which gaseous reaction products are involved.

Composite propellants are composed of crystalline oxidizer particles dispersed in polymeric fuel binder. Ballistic modifiers are incorporated in the formulation to achieve required burn rates. AP is used as the most common oxidizer and hydroxyterminated polybutadiene (HTPB) as the fuel binder. The ballistic modifiers play a significant role in determining the burn rate law of composite propellants. The ballistic modifiers are reported to influence AP-binder decomposition Pattern which is proposed to control the combustion behavior of the propellant.

Now recently metals are introduced as more efficient catalysts as compared to metal oxides. There is continuous interest in the synthesis and application of nanometer particles of metal or metal oxides, due to their large specific surface area and high activity in most catalytic processes. It is noted that these nanoparticles are not only effective in the gas–solid, gas–liquid–solid or liquid–solid catalytic processes, where the nanoparticles as the catalysts are the solid phase, but also are effective in the solid–solid catalytic processes. For instance, the nanosized metal oxide particles have been proved effectively in improving the decomposition or explosion of the AP, a key energetic material and the most common oxidizer in the rocket propellant. However, considering the limited loading of AP or their composites in the rocket, it is crucial to further improve its decomposition efficiency to produce large amount of energy as far as possible and to decrease its burning temperature for easy operation and control. In contrast to the nanoparticles of metal oxide, the pure metal nanoparticles are much sensitive to the oxygen and can be effective in improving the decomposition efficiency of AP.

## Acknowledgments

The authors are grateful to Chemistry Department of KSKV University, Bhuj for laboratory facility. One of the authors Shalini Chaturvedi is also thankful to CSIR for Research associate (RA) fellowship.

## References

Ball, P., Garwin, L., 1992. Science at the atomic scale. *Nature* 355, 761.  
Baumer, M., Freund, H.J., 1999. Metal deposits on well-ordered oxide films. *Prog. Surf. Sci.* 61, 1271.

Biju, V., Abdul Khader, M., 2003. Molecular and biomolecular spectroscopy. *Spectrochim. Acta A* 59, 121.  
Bircumshaw, L., Newman, B., 1955. Thermal decomposition of ammonium perchlorate. *Proc. Roy. Soc. A* 227, 228.  
Boldyrev, V.V., 2006. Thermal decomposition of ammonium perchlorate. *Thermochim. Acta* 443, 1–36.  
Boldyrev, V.V., Savintsev, Yu.P., Mulina, T.V., Shchetinina, G.V., 1970. On the physicochemical reasons of the formation and growth of reaction nuclei during thermal decomposition of ammonium perchlorate. *Kinetika i kataliz* 11 (B.5), 1131.  
Brill, T.B., Budenz, B.T., 2000. Progress in aeronautics and astronautics. In: Yang, V., Brill, T.B., Ren, W.Z. (Eds.), *American Institute of Aeronautics and Astronautics*, vol. 185, Chapter 1.1, Solid Propellant Chemistry, Combustion and Motor Interior Ballistics, pp. 3–32.  
Buzea, C., Pacheco, I., Robbie, K., 2007. Nanomaterials and nanoparticles: sources and toxicity. *Biointerphases* 2, 17.  
Carnes, C.L., Klabunde, K.J., 2003. The catalytic methanol synthesis over nanoparticle metal oxide catalysts. *J. Mol. A: Catal. Chem.* 194, 227.  
Chakravarthy, S.R., Price, E.W., Sigman, R.K., 1997. Characterisation of heterogeneous solid propellants. *J. Prop. Power* 13 (4), 471.  
Chen, D.-H., Hsieh, C.-H., 2000. *J. Mater. Chem.* 12, 1345.  
Chen, W., Li, F., Liu, J., Song, H., Yu, J., 2005. Preparation of nanocrystalline  $\text{Co}_3\text{O}_4$  and its catalytic performance for thermal decomposition of ammonium perchlorate. *J. Catal.* 12, 1073.  
Chen, W., Li, F., Liu, J., Song, H., Yu, J., 2005. Preparation of nanocrystalline  $\text{Co}_3\text{O}_4$  and its catalytic performance for thermal decomposition of ammonium perchlorate. *J. Catal.* 12, 1073.  
Cheng, Z., Xu, J., Zhong, H., Yi, Y., Li, F., 2010. *Rare Metal* (1), 32.  
Dotson, R.L., 1993. A novel electrochemical process for the production of ammonium perchlorate. *J. Appl. Electrochem.* (9), 897.  
Duan, H., Lina, X., Liua, G., Xua, L., Li, F., 2008a. Synthesis of Ni nanoparticles and their catalytic effect on the decomposition of ammonium perchlorate. *J. Mater. Proc. Tech.* 208, 494.  
Duan, H., Lin, X., Liu, G., Xu, L., Li, F., 2008b. Synthesis of Co nanoparticles and their catalytic effect on the decomposition of ammonium perchlorate. *Chin. J. Chem. Eng.* (2), 325.  
Dubovitsky, A.V., Buben, N.Ya., Manelis, G.B., 1964. Investigation of the movement of  $\text{NH}_4^+$  ion in ammonium perchlorate by means of electron paramagnetic resonance. *Russ. J. Struct. Chem.* 5, 40–43.  
Edelstein, A.S., Cammarata, R.C., 1998. *Nanomaterials: Synthesis, Properties and Applications*, 2nd ed. CRC Press.  
Edwards, P.P., Johnston, R.L., Rao, C.N.R., Braunstein, P., Oro, G., Raithby, P.R., 2000. *Metal Clusters in Chemistry*. Wiley-VCH, New York.  
Evans, M.W., Beyer, R.B., McCulley, L., 1964. Initiation of deflagration waves at surfaces of ammonium perchlorate–copper chromite–carbon pellets. *J. Chem. Phys.* (9), 2431.  
Feldmann, C., Jungk, H.,-O. Int. Ed. 2001. Polyol-mediated preparation of nanoscale oxide particles. *Angew. Chem.* 40, 359.  
Fernandez-Garcia, M., Martinez-Arias, A., Hanson, J.C., Rodriguez, J.A., 2004. Nanostructured oxides in chemistry: characterization and properties. *Chem. Rev.* 104, 4063.  
Ferrando, R., Jellinek, J., Johnston, R.L., 2008. Nanoalloys: from theory to applications of alloy clusters and nanoparticles. *Chem. Rev.* (3), 845.  
Fievet, F., Lagier, J.P., Blin, B., Beaudoin, B., Figlarz, M., 1989. Homogenous and heterogenous nucleations in the polyol process for the preparation of micron and submicron size metal particles. *Solid. State Ion.* (32/33), 198.  
Foltz, M., Meinschein, J., 1995. Ammonium perchlorate phase transitions to 26 GPa and 700K in diamond anvil cell. *Mater. Lett.* (6), 407.  
Gleiter, H., 1995. Nanostructured materials state of the art and perspectives. *Nanostruct. Mater.* 6, 3.

- Gromov, A., Strokova, Y., Kabardin, A., Vorozhtsov, A., Teipel, U., 2009. Experimental study of the effect of metal nanopowders on the decomposition of HMX AP and AN. *Prop. Expl. Pyrotech.* 34 (6), 506.
- Hall, A.R., Pearson, G.S., 1967. Ammonium perchlorate. A review of its role in composite propellant combustion, Rocket Propulsion Establishment. Westcoff Technol. Report no. 67/1, 164.
- Ibers, J.A., 1960. Nuclear magnetic resonance study of polycrystalline  $\text{NH}_4\text{ClO}_4$ . *J. Chem. Phys.* 32, 1448.
- Ivanov, E.Yu., Boldyrev, V.V., 1979. On the mechanism of polymorphous transition in ammonium perchlorate crystals. *Dokl. AN SSSR* (4), 862.
- Jacobs, P., Kureishy, A., 1962. The effect of additives on thermal decomposition of ammonium perchlorate. Eighth Symp. Combust The Williams and Wolkins Co Baltimore. 672.
- Jacobs, P.W.M., Ng, W.L., 1974. Thermal decomposition of ammonium perchlorate single crystals. *J. Solid State Chem.* (4), 305.
- Jacobs, P.W.M., Pearson, G.S., 1969. The thermal decomposition of ammonium perchlorate(i) introduction experimental analysis of gaseous products and thermal decomposition experiments. *Combust. Flame* 13, 419.
- Jacobs, R.V., Russel-Jones, A.A., 1967a. On the mechanism of decomposition of ammonium perchlorate. *Raketnaya tekhnika i kosmotavtika* (4), 275 (in Russian).
- Jacobs, R.V., Russel-Jones, A.A., 1967b. Thermal decomposition of  $\text{NH}_4\text{ClO}_4$ , combustion and explosion. *Raketnaya Tekhnika i Kosmotavtika* 5, 275.
- Jacobs, P.W.M., Whithead, H.M., 1969. Thermal decomposition and combustion of ammonium perchlorate. *Chem. Rev.* 4, 551.
- Kaidymov, B.I., Gavazova, V.S., 1974a. The influence of polymorphous transition in ammonium perchlorate on the catalytic effect of homogeneous and heterogeneous additives in its thermal decomposition. *Fizika goreniya i vzryva* (6), 801 (in Russian).
- Kaidymov, B.I., Gavazova, V.S., 1974b. A sharp change in the inhibiting effect of ammonia on thermal decomposition of ammonium perchlorate as a result of its phase transition. *J. Inorg. Nucl. Chem.* (12), 3848.
- Keenan, A.G., Siegmund, R.F., 1969. Thermal decomposition of ammonium perchlorate. *Quart. Rev. Chem. Soc. London* (3), 435.
- Kishore, K., Sunitha, M.R., 1979a. Comprehensive view of the combustion models of composite solid propellants. *AIAA J.* (11), 1216.
- Kishore, K., Sunitha, M.R., 1979b. Effect of transition metal oxides on decomposition and deflagration on composite solid propellant systems: a survey. *AIAA J.* 17, 1118.
- Kurihara, L.K., Chew, G.M., Schoen, P.E., 1995. Nanocrystalline metallic powders and films produced by the polyol method. *Nanostrut. Mater.* 5, 607.
- Liu, L., Li, F., Tan, L., Li, M., Yang, Y., 2004a. Effects of metal and composite nanopowders on the thermal decomposition of ammonium perchlorate (AP) and the ammonium perchlorate/ hydroxy-terminated polybutadiene (AP/HTPB) composite solid propellant. *Chin. J. Chem. Eng.* (4), 595.
- Liu, L., Li, F., Tan, L., Ming, L., Yi, Y., 2004b. Effects of nanometer Ni, Cu, Al and NiCu powders on the thermal decomposition of ammonium perchlorate. *Prop. Expl. Pyrotech.* 29 (1), 34.
- Liu, Z.-T., Li, X., Liu, Z.-W., Lu, J., 2009. Synthesis and catalytic behaviors of cobalt nanocrystals with special morphologies. *Powder Tech.* 189, 514.
- Lw, L., Wu, Y., Shi, Y., Hu, C., 2004. Synthesis and characteristics of NiO nanowire by a solution method. *Mater. Lett.* 58, 2700.
- Ma, Z., Li, F., Chen, A., Bai, H., 2004. Preparation and thermal decomposition behavior of  $\text{Fe}_2\text{O}_3$ /ammonium perchlorate composite nanoparticles. *Acta Chim. Sin.* 13, 1252.
- Manelis, G.B., Ed., 1981. Chernogolovka. Mechanism of thermal decomposition of ammonium perchlorate: a collection of papers. Institute of Chemical Physics AN SSSR, pp. 1–129.
- Michael Hogan, C., 1969. Density of states of an insulating ferromagnetic alloy. *Phys. Rev.* 188 (2), 870.
- Pavlyuchenko, M.M., Prodan, E.A., Peshrovskaya, L.I., 1977. On the effect of temperature on the rate of topochemical transformations in ammonium perchlorate. *Russ. J. Phys. Chem.* 51 (3), 577.
- Peiris, S.M., Pangilinan, G.I., Russell, T.P., 2000. Structural properties of ammonium perchlorate compressed to 5.6 GPa. *J. Phys. Chem. A* 104, 11188.
- Ping, C., Li, F., Jian, Z., Wei, J., 2006. Preparation of Cu/CNT composite particles and catalytic performance on thermal decomposition of ammonium perchlorate. *Prop. Expl. Pyrotech.* (6), 452.
- Raevsky, A.V., Manelis, G.B., 1963. On the mechanism of decomposition of ammonium perchlorate. *Dokl. AN SSSR* 151 (4), 886.
- Rodriguez, J.A., Liu, G., Jirsak, T., Herbek, Chang, Z., Dvorak, J., Mati, A.J., 2002. Activation of gold on titania: adsorption and reaction of  $\text{SO}_2$  on Au/ $\text{TiO}_2(110)$ . *Am. Chem. Soc.* 124, 5247.
- Rosser, W.A., Inami, S.H., Wise, H., 1968. Thermal decomposition of ammonium perchlorate. *Combust. Flame.* 12, 427.
- Said, A.A., Al-Qusami, R., 1996. The role of copper cobaltite spinel,  $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$  during the thermal decomposition of ammonium perchlorate. *Thermochim. Acta* 83, 275.
- Saravanan, P., Jose, T.A., John Thomas, P., Kulkarni, G.U., 2001. Submicron particles of Co, Ni and Co–Ni alloys. *Bull. Mater. Sci.* 24, 515.
- Savintsev, Yu.P., Mulina, T.V., Boldyrev, V.V., 1972. Thermal decomposition of  $\text{NH}_4\text{ClO}_4$  Combustion and explosion. *Moscow auka.* 756–59.
- Shufen, L., Zhi, J., Shuqin, Y., 2002. Thermal decomposition of HMX influenced by nano-metal powder. *Fuel Chem.* (2), 596.
- Singh, G., Felix, S.P., 2003. Evaluation of transition metal salts of NTO as burning rate modifier for HRPB-AN composite solid propellants. *Combust. Flame.* 132, 422.
- Singh, N.B., Ojha, A.K., 2002. Formation of copper oxide through  $\text{NaNO}_3\text{--KNO}_3$  eutectic melt and its catalytic activity on thermal decomposition of ammonium perchlorate. *Thermochim. Acta* 67, 390.
- Singh, G., Pandey, D.K., 2002. Studies on energetic compound: part 24-haxamine metal perchlorate as high energetic burning rate catalysts. *J. Energy Mater.* 20, 223.
- Singh, G., Kapoor, I.P.S., Dubey, S., Siril, P.F., Hua, Yi, J., ZHAO, F.Q., HU, R.-Z., 2008. Effect of mixed ternary transition metal ferrite nanocrystallites on thermal decomposition of ammonium perchlorate. *Thermochem. Acta* 477, 42.
- Singh, G., Kapoor, I.P.S., Dubey, S., 2009a. Bimetallic nanoalloys: preparation, characterization and their catalytic activity. *J. Alloys Comp.* 480, 270.
- Singh, G., Kapoor, I.P.S., Dubey, S., Siril, P.F., 2009b. Kinetics of thermal decomposition of ammonium perchlorate with nanocrystals of binary transition metal ferrites. *Prop. Expl. Pyro.* 34, 72.
- Singh, G., Kapoor, I.P.S., Dubey, S., Siril, P.F., 2009c. Preparation, characterization and catalytic activity of transition metal oxide nanocrystals. *J. Sci. Conf. Proc.* 1, 11.
- Solymosi, F., 1977. Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase. *A kademiai Kiado, Budapest*, p. 195.
- Song, M., Chen, M., Zhang, Z., 2008a. Effect of Zn Powders on the Thermal Decomposition of Ammonium Perchlorate. *Prop. Expl. Pyrotech.* (4), 261.
- Song, M.-R., Chen, M., Zhan, Z.-J., 2008b. *Mater. Char.* (5), 514.
- Svetlov, B.S., Koroban, V.A., 1967. On the inhibition of thermal decomposition of ammonium perchlorate by the products of decomposition. *Kinetika i kataliz* 8, 456.
- Svetlov, B.S., Koroban, V.A., 1970. On the mechanism of thermal decomposition of ammonium perchlorate. *Fizika goreniya i vzryva* (1), 12 (in Russian).
- Tan, L.H., Li, Q.H., Yang, Y., Li, F.S., Liu, L.L., Li, M., 2004. Study on the preparation and catalytic characteristics of nano-nickel. *J. Solid Rocket Technol.* (27), 198.

- Tang, C., Li, L., Gao, H., Li, G., Qiu, X., Liu, J., 2009. *J. Power Source* 188 (2), 397.
- Tao, D.L., Wei, F., 2004. New procedure towards size-homogeneous, 1. and well-dispersed nickel oxide nanoparticles of 30 nm. *Mater. Lett.* 58, 3226.
- Trudeau, M.L., Ying, J.Y., 1996. Nanocrystalline materials in catalysis and electrocatalysis: structure tailoring and surface reactivity. *Nanostruct. Mater.* 7, 245.
- Valden, M., Lai, X., Goodman, D.W., 1998. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. *Science* 281, 1647.
- Vinod, C.P., Kulkarni, G.U., Rao, C.N.R., 1998. Size-dependent changes in the electronic structure of metal clusters as investigated by scanning tunneling spectroscopy. *Chem. Phys. Lett.* 289, 329.
- Vogt H., Balej J., Bennett J. E., Wintzer P., Sheikh S. A., Gallone P. 2002. Chlorine Oxides and Chlorine Oxygen Acids. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH. DOI:10.1002/14356007.a06\_483.
- Wang, Y., Zhu, J., Yang, X., Lu, L., Wang, X., 2005. Preparation of NiO nanoparticles and their catalytic activity in the thermal decomposition of ammonium perchlorate. *Thermochim. Acta* 437, 106.
- Zhi, J., Feng-Qi, Z., 2002. Study on effects of nanometer metal powder on thermal decomposition of HMX. *J. Prop. Tech.* 23, 258.
- Zhi, J., Tian-Fang, W., Shu-Fen, L., Feng-Qi, Z., Zi-Ru, L., Cui-Mei, Y., Yang, L., Shang-Wen, L., Gang-Zhui, Z., 2006. *J. Therm. Anal. Calc.* 85 (2), 315.
- Zhu, J., Chen, H., Xie, B., Yang, X., Lu, L., Wang, X., 2002. *Chin. J. Catal.* 25, 637.
- Zhu, J., Zhang, W., Wang, H., Yang, X., Lu, L., Wang, X., 2004. *Chin. J. Inorg. Chem.* 20, 863.