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Synthesis, Characterization and Applications of Iron Oxide Nanoparticles – a Short Review

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ABSTRACT: Iron oxide is a mineral compound that shows different polymorphic forms, including hematite (α-Fe_2O_3), magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). Solid propulsion technology nanoparticulate materials, such as hematite and maghemite, exhibit high performance on thermal decomposition of ammonium perchlorate. The enhanced catalytic effect of metallic iron oxide nanoparticles is attributed to their particle size, more active sites and high surface area, which promotes more gas adsorption during thermal oxidation reactions. Nowadays, metallic iron nanoparticles can be synthesized via numerous methods, such as co-precipitation, sol-gel, microemulsion, or thermal decomposition. Although there are data on these synthetic methods in the literature, there is a lack of details related to nanoparticulate oxides and to their characterization techniques. In this context, this short review based on scientific papers, including data from the last two decades, presents methods for obtaining nanoparticulate iron oxides as well as the main aspects of the different characterization techniques and also about the decomposition aspects of these nanomaterials. Morphologies and structures of iron oxides can be characterized through transmission electron microscopy, scanning electron microscopy, X-ray powder diffraction, and Fourier transform infrared spectroscopy. As for textural properties, they are usually determined by physical adsorption techniques.

KEYWORDS: Iron oxide nanoparticles, Synthesis, Applications, Characterization techniques, Ammonium perchlorate.

INTRODUCTION

In the last two decades, nanotechnology has attracted great interest in several areas of research for the development of nanoscale materials which can be obtained through different techniques, such as physical or chemical methods. Due to their size (diameters ranging from 1 to 100 nm) nanoparticles present specific and controllable properties that are different from those they present on the macroscopic scale thus enabling unique applications (Duran *et al.* 2006; Yetter *et al.* 2009; Srivastava *et al.* 2009). The change in properties is due to two main effects: (i) surface effects or size reduction effect (when particle size is reduced, a greater proportion of atoms are found at the surface); (ii) quantum confinement-modification in electronic structure (Srivastava et al. 2009; Gupta and Gupta 2005).

It is known that the ratio between the number of surface atoms and the number of massive atoms increases significantly with particle size reduction. As the surface atoms have less coordination in relation to massive atoms, nanostructured materials exhibit significantly different physical, chemical, optical, mechanical, electrical and also magnetic properties (Chaturvedi *et al.* 2012; Yetter *et al.* 2009). The excess of energy of surface atoms contributes for many of the extraordinary characteristics of nanoparticles (Yetter *et al.* 2009). This way, nanoscale materials present great potential for applications in several technological areas such as nanoelectronics and computer technology, medicine, aeronautics and space exploration, biotechnology and agriculture (Srivastava *et al.* 2009).

In recent years, nanoscale transition of metallic oxides, such as iron oxide, including hematite, magnetite, and maghemite, has been attracting growing interest as they exhibit unique electrical,

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optical and magnetic properties for numerous applications such as production of inorganic pigments, magnetic storage media, development of gas sensors as well as electronic and optical devices, information storage, color imaging, magneto caloric refrigeration, bioprocessing, ferrofluid technology and wastewater treatment adsorbents (Xu *et al.* 2008, Gregor *et al.* 2010; Moahapatra and Anand 2010).

Iron oxide also plays an important role in aerospace industry, as it has been incorporated in composite propellant to improve its burning rate. Because the combustion mechanism of propellants is highly dependent on decomposition of ammonium perchlorate (NH_4ClO_4 or AP), nowadays there are many studies concerning the catalytic effect of nano-Fe_2O_3 on thermal decomposition of ammonium perchlorate.

IRON OXIDES

Iron oxide is a mineral compound which occurs abundantly in nature. It presents more than one crystal structure and also different structural and magnetic properties (Cornell and Schwertmann 2000; Machala *et al.* 2011).

The main forms of these minerals are hematite, magnetite and maghemite (Babay *et al.* 2015; Cornell and Schwertmann 2000). Crystal structure of the three oxides can be defined in terms of close packed planes of oxygen anions with iron cations in octahedral or tetrahedral interstitial sites (Cornell and Schwertmann 2000; Zboril *et al.* 2002; Teja and Koh 2009; Babay *et al.* 2015).

Because of its polymorphism (Babay *et al.* 2015), magnetite (Fe_3O_4) is one of the most interesting crystallographic phases of iron oxide, especially in its nanosized forms. It exhibits four different crystalline polymorphs with unique magnetic properties. The main forms, hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3), occur in nature and the other oxides in the forms beta (β-Fe_2O_3) and epsilon (ε-Fe_2O_3) are nanometric structures which are generally synthesized in laboratory (Machala *et al.* 2011).

Hematite, α-Fe_2O_3, is the most known of iron oxides and the most frequent polymorph which exists in nature as mineral (Zboril *et al.* 2002; Machala *et al.* 2011), occurring widely in rocks and soils. It is an oxide with a weak ferromagnetic or anti-ferromagnetic behavior at room temperature. Furthermore, above 956 K (Curie or Curie temperature or Néel temperature or Curie-Weiss law) (Teja and Koh 2009; Zboril *et al.* 2002), it is paramagnetic. α-Fe_2O_3 exhibits corundum type and rhombohedral structure which is made up of an ion O^{-2} reticle as a close-packed hexagonal crystallographic system and Fe^{+3} ions occupying two-thirds of the octahedral interstices in alternate layers (Zboril *et al.* 2002; Machala *et al.* 2011). Hematite is easier to synthesize than the other forms of oxide as it is the end product of other iron oxide forms of transformation and is also extremely stable under environmental conditions (Machala *et al.* 2011; Cornell and Schwertmann 2000; Teja and Koh 2009).

Maghemite (γ-Fe_2O_3), a typical ferromagnetic mineral (Zboril *et al.* 2002; Oliveira *et al.* 2013), is thermally unstable and is transformed to hematite at higher temperatures (Zboril *et al.* 2002). It has a spinel crystal structure which is similar to that of magnetite, except of vacancies in cation sublattice. Two-thirds of the sites are filled with Fe (III) ions arranged regularly with two filled sites being followed by one vacant site. γ-Fe_2O_3 as well as magnetite (Fe_3O_4) are easily magnetized and thus present high magnetic response when submitted to an external magnetic field (Cornell and Schwertmann 2000; Teja and Koh 2009). They are metastable oxides in the oxidative atmosphere and so they are oxidized to α-Fe_2O_3 when heated to a temperature above 673 K (Xu *et al.* 2008).

β-Fe_2O_3 is a rare kind of iron oxide that exhibits a body-centered cubic structure: Fe^{+3} ions that occupy two non-equivalent octahedral crystallographic sites. It is the only iron oxide form which presents a paramagnetic behavior at room temperature. Its Néel magnetic transition temperature is between 100 and 119 K; below this temperature, β-Fe_2O_3 is anti-ferromagnetically arranged. As it is thermodynamically unstable, it is transformed into either α-Fe_2O_3 or γ-Fe_2O_3 when heated (Machala *et al.* 2011).

The epsilon form (ε-Fe_2O_3) of iron oxide presents an orthorhombic crystal structure derived from the close-packing of four layers of oxygen. ε-Fe_2O_3 can be regarded as a polymorphous intermediate presenting similarity to both γ-Fe_2O_3 and α-Fe_2O_3. Although its magnetic behavior is not fully understood, what is known is that ε-Fe_2O_3 undergoes two magnetic transitions – one occurring near 495 K (Curie temperature) and the other at 110 K. In the first one, ε-Fe_2O_3 goes from a paramagnetic to a magnetically ordered state while at 110 K it undergoes a transition to a magnetic regime, quite different from that observed at room temperature (Machala *et al.* 2011).

Magnetite (Fe_3O_4), at room temperature, presents ferromagnetic properties (Teja and Koh 2009), which differs from other iron oxides forms as its structure has both bivalent and trivalent iron. It presents a crystal structure as inverse spinel, which is formed by stacking plans as polyhedral model and it has a face-centered cubic unit cell based on 32 O^{-2} ions, as the formula Fe (III)[Fe (II), Fe (III)]O_4, and the Fe (III) ions are randomly distributed between octahedral and tetrahedral sites with Fe (II) ions occupying the octahedral sites (Cornell and Schwertmann 2000).

One of the most important objectives of the study of iron's solid chemistry state is to understand the mechanisms and the kinetics of polymorphous transformation (kinetics of the transition crystaline phase) (Callister Jr 2012) of iron oxides. Besides, these issues use to control these processes, mainly because different polymorphic states present particular properties and a range of potential applications in several fields (Machala *et al.* 2011).

METHODS OF PREPARATION

Over the last decades many method syntheses have been developed in order to obtain iron oxides, α-Fe_2O_3, Fe_3O_4, and γ-Fe_2O_3, on nanometric scales for application in distinct technological areas. The most common methods include co-precipitation, sol-gel, microemulsion and thermal decomposition (Teja and Koh 2009; Cheng *et al.* 2012).

The major technological challenge of synthesis methods is controlling the nanoparticles characteristics, such as crystallinity, size and shape, polydispersity, porosity and morphology. Indeed, these structural characteristics are greatly influenced by reaction parameters and may have a critical influence on electrical, mechanical, optical and magnetic properties, which, in turn, determine the behavior of nanometric iron oxide for different applications (Gupta and Gupta 2005; Moahapatra and Anand 2010; Chaturvedi *et al.* 2012).

CO-PRECIPITATION

Magnetic nanoparticles of iron oxides magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) can be synthetized through the co-precipitation of a stoichiometric mixture of Fe (II) and Fe (III) salts in a basic aqueous medium of sodium hydroxide (NaOH) or ammonium hydroxide (NH_4OH) (Sun and Zeng 2002). Particles from 5 to 20 nm in diameter can be prepared by this synthesis method. Experimental conditions are critical and depend on the type of ion salt-chlorides, sulphates, nitrates or perchlorates and also on the Fe^{2+} / Fe^{3+} concentration ratio. Other synthesis parameters, such as pH, ionic force of the medium and reaction temperature, can be adjusted in the synthesis in order to control the size of magnetic iron oxide nanoparticles characteristics or surface properties (Wu *et al.* 2008; Gupta and Gupta 2005).

SOL-GEL

Sol-gel synthesis methods usually refer to hydrolysis and condensation of metal alkoxides or alkoxide precursors, resulting in dispersions of oxide particles in "sol", which is then dried or gelled by removing the solvent or by chemical reaction (Teja and Koh 2009).

Due to their large surface-to-volume ratio, magnetic iron oxide nanoparticles possess high surface energies and therefore tend to agglomerate and form clusters thus resulting in increased particle size. Moreover, the naked iron oxide particles have high chemical activity and are easily oxidized in air, generally leading to loss of magnetism and dispersibility. A strategy to prevent agglomeration is to promote the modification of surface nanoparticles by coating them with organic molecules, polymers, biomolecules or inorganic molecules, such as silica. Various polymers such as poly(vinyl alcohol), poly(lactide-co-glycolide), polyethyleneimine, polymethylmethacrylate and poly(ethylene glycol) as well as natural polymeric systems or proteins including gelatin, chitosan and dextrosan have been applied. Among inorganic coatings, silica, carbon and precious metals such as gold, silver and platinum are commonly used (Wu *et al.* 2008; Gupta and Gupta 2005).

The solvent used in the sol-gel method is generally water and the precursors can be hydrolyzed by either an acid or a base. Reaction rates, temperature, nature of precursors and pH are parameters that affect the structures and size of iron oxide (Teja and Koh 2009), for example, nanomaghemite, γ-Fe_2O_3 with particle size from 6 to 15 nm after heat treatment at 673 K (Laurent *et al.* 2008; Teja and Koh 2009).

MICROEMULSION

The pioneering work on microemulsion started in 1943, but in 1959 the concept of microemulsion became known by Hoar and Schulman and since then its use has grown. According to the authors, microemulsions are a transparent system formed spontaneously when oil phase and aqueous phase are mixed in relatively large amounts of ionic surfactant containing a medium chain alcohol (C_5-C_{10}) (Rosano *et al.* 1988).

Microemulsion method has been widely used to synthesize catalytic iron oxide because it yields particles within a narrow pore size distribution ranging from 4 to 15 nm with cubic or spherical morphology (Gupta and Gupta 2005) and high surface area (315 $m^2.g^{-1}$) (Bumajdad *et al.* 2011).

The preparation of magnetic iron oxide nanoparticles with controlled size and morphology has been carried out in water-in-oil microemulsion consisting of a cationic or non-ionic surfactant (Triton-X), a co-surfactant (glycols, hexanol, 1-butanol), oil phase (n-octane, cyclohexane) and aqueous phase (Fernandes *et al.* 2013). The microemulsion is formed through addition of an aqueous solution with iron salt precursors to the surfactant/co-surfactant mixture.

Magnetic nanoparticles are produced by adding a precipitating agent such as ammonia to the microemulsion containing the iron precursors while agitating. It was observed that the nanoparticles agglomeration process during synthesis depends on experimental parameters, such as temperature, pH, reaction medium, washing cycles, among others (Wu *et al.* 2008; Bumajdad *et al.* 2011). Some works reported the iron oxide nanoparticles preparation through water-in-oil microemulsion route by mixing appropriate amounts of ammonia solution or tetrabutylammonium hydroxide as precipitants (Bumajdad *et al.* 2011). The method includes cationic surfactants as di-n-dodecyldimethylamonium bromide and non-ionic surfactants as polyoxyethylene in aqueous solution of tetrabutylammonium hydroxide. Results showed that the surfactant concentration and also the water-to-surfactant molar ratio have no effect on the crystallite structure of the iron oxide, but, instead, they clearly affect nanoparticles morphology such as pore volume and shape, surface area and crystallite size (Bumajdad *et al.* 2011).

Among various synthesizing methods of iron oxide nanoparticles water-in-oil microemulsion methods have been of a great interest to precisely control the size and size distribution of various nanoparticles (7 – 10 nm) (Maleki *et al.* 2012). Not only, microemulsions show a great variety of structures, such as globular, spherical aggregates, bi-continuous and tubular bi-continuous (Okoli *et al.* 2012; Wu *et al.* 2008; Oliveira *et al.* 2004) with particle diameters under 1400 Å, typically in the order of 100 Å (Oliveira *et al.* 2004).

In recent years, magnetic iron oxide nanoparticles have been encapsulated with silica precursor, which can significantly increase the stability of nanoparticles, protecting them from oxidation and also reducing any toxic effects of them (Laurent and Mahmoudi 2011). It can be achieved by using different methods which consist of hydrolysis of alcoxysilane as tetraethoxysylane (TEOS) (Fernandes *et al.* 2013; Teja and Koh 2009; Laurent and Mahmoudi 2011), in the presence of ammonia and superparamagnetic iron oxide nanoparticles. This precursor with the formula $Si(OC_2H_5)_4$ contains four ethyl groups attached to SiO_4, which is called orthosilicate (Fernandes *et al.* 2013).

THERMAL DECOMPOSITION

The method of thermal decomposition of precursors, such as ferric (III) acetylacetonate, iron nitrosophenylhydroxylamine or iron pentacarbonyl in octyl ether and oleic or lauric acid followed by oxidation, leads to formation of iron oxide nanoparticles with size distribution between 4 and 16 nm. The reaction of ferric (III) acetylacetonate in phenyl ether at 538 K in the presence of alcohol, oleic acid and oleyamine produces Fe_3O_4 nanoparticles that may easily be transformed in γ-Fe_2O_3 by annealing at 523 K and oxygen for 2 h. Thermal decomposition of nitrosophenylhydroxylamine produces iron nanoparticles which, after oxidation with reactants such as trimethylamine oxide, form monodispersed nanoparticles of γ-Fe_2O_3. This preparation method produces monodispersed particles with a narrow size distribution, but has a great disadvantage that the resulting particles are always dissolved in non-polar solvents (Wu *et al.* 2008).

It should be pointed out that many of the nanostructured iron oxide properties depend on the methods of preparation, as they have a significant importance on material particle size and forms, size distribution, surface chemistry and therefore on their applications. Furthermore, the method of preparation also dictates the level of structural defects, their distribution and the possible presence of impurities on iron oxide (Teja and Koh 2009).

APPLICATION IN CATALYTIC REACTIONS

Since pollution from heavy metals has been one of the most serious environmental problems over the last years, various methods for heavy metal removal from wastewater have been studied. Therefore, considerable attention has been paid to removal of heavy metals such as Pb^{+2} ions from industrial wastewater, by utilizing adsorption process with different adsorbents, such as activated charcoal, polymeric adsorbents, metal oxides and bioadsorbents (Cheng *et al.* 2012). Among these, adsorbents based on magnetic nanomaterials such as maghemite (γ-Fe_2O_3) with particle size of 60 nm have distinguished themselves due to their single properties such as large area-to-volume ratio, diminished consumption of chemicals and also absence of secondary pollutants (Cheng *et al.* 2012).

In catalysis, chemical reactions in solid, liquids or gases are accelerated through the introduction of a solid phase, whose surface must contain a great number of active sites so that the reactants may adsorb, react and then desorbs. As the optimization of a catalyst requires increase in the numbers of active sites to increase the surface area, its particle size should be small (typically 10 – 80 nm) (Chaturvedi *et al.* 2012).

Therefore, in modern laboratories, catalysts typically consist of nanometer sized-particles supported on nanometer-sized pores or structural features. Indeed, nanomaterials are more effective than conventional catalysts because of two reasons: first, their extremely small particle size (typically 10 – 80 nm) provides an excellent surface area-to-volume ratio (Chaturvedi *et al.* 2012). Next, when materials are fabricated on the nanoscale, they show properties not found within their macroscopic counterparts (Chaturvedi *et al.* 2012; Gregor *et al.* 2010). In a study on the catalytic efficiency of iron oxide (α-Fe_2O_3) nanoparticles in hydrogen peroxide decomposition results suggested that, besides the catalytic effect of the high surface area, there is a more complex factor – the surface quality of the catalyst driving their efficiency. In addition to the main effect of the sample's crystallinity, other qualitative parameters such as the chemical composition and particle morphology of catalysts are important. As a consequence, iron oxides hematite, magnetite and maghemite are extensively used in the catalysis of a number of reactions such as the synthesis of styrene, photocatalytic production of hydrogen and oxygen, removal of carbon monoxide, catalytic conversion of methane in aromatic compounds, thermal decomposition of ammonium perchlorate as well as in water treatment, catalytic decomposition of hydrogen peroxide, fuel cells and production of biodiesel (Chaturvedi *et al.* 2012; Weddemann *et al.* 2010; Teja and Koh 2009; Gregor *et al.* 2010).

The chemical properties of many crystal surfaces, especially oxides, are significantly influenced by their structural defects which are deviations from the spatial arrangements of the atoms, ions or molecules in their crystalline structures. Defects can be conveniently classified according to their spatial extension as dot, line or plane defects. In fact, impurities on the surface, interstices, vacancies or adsorbates are often preferred adsorption sites and hence are particularly chemically active. Many defects exhibit special electronic structures which promote special properties on the surface. In addition, electrically charged defects enable the electron transfer process which plays an important role in chemical reactions, mainly in heterogeneous catalysis (Koning *et al.* 2011).

THERMAL COMBUSTION

Iron oxides are commonly applied as ballistic additives in composite solid propellant formulations in order to accelerate the combustion at the burning surface and so to increase the propellant burn rate and its thrust-time curve. This way, they permit burning rate tailoring to fit a specific grain design. Since the combustion mechanism of propellants is very much dependent upon the decomposition of ammonium perchlorate, there are many studies concerning the catalytic effect of nanosized ferric oxide on thermal decomposition of the oxidizer (Ma *et al.* 2006; Joshi *et al.* 2008; Fujimura and Miyake 2010).

In the field of solid propulsion, nanosized transition metallic oxides such as iron oxide, hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) are materials that stand out as burn catalysts in thermal combustion reactions (Joshi *et al.* 2008; Chaturvedi *et al.* 2012; Patil *et al.* 2006).

Ammonium perchlorate is the most used oxidizer in composite solid propellant formulations; however, its decomposition mechanism is not fully understood in literature. Indeed, the decomposition of ammonium perchlorate is rather complicated mainly because this simple molecule consists of four different elements (Joshi *et al.* 2008; Chaturvedi *et al.* 2012). The most important crystalline transitions of ammonium perchlorate are: orthorhombic at temperature below 513 K and cubic one, which is stable at temperatures above 513 K (Boldyrev 2006). The thermal decomposition of ammonium perchlorate involves complex physical and chemical reactions, which occur in two main decomposition regions. In the first region, at a temperature below 623 K, endothermic reactions take place with a fast reaction between ammonia and perchloric acid forming side products such as oxygen (O_2), dinitrogen oxide (N_2O), chlorine (Cl_2) and nitrogen monoxide (NO). The second phase of decomposition, above 623 K, corresponds to exothermic reactions with the release of volatile products such as N_2O, NO, Cl_2 and H_2O (Joshi *et al.* 2008; Chaturvedi and Dave 2013).

Since several studies are being carried out to clarify the mechanisms of thermal decomposition of ammonium perchlorate, there were at least three points of view in relation to the elementary stages of the decomposition process. However the matter is still under discussion, some researchers have demonstrated that the decomposition of ammonium perchlorate occurs through an electron transfer mechanism from a ClO_4^- anion to a NH_4^+ cation (Boldyrev 2006). Taking into account that ammonium perchlorate has dielectric characteristics and also that it presents low decomposition temperature, *i.e.*

below 623 K, this mechanism would be unlikely. Another proposed mechanism would be by rupture of the chlorine – oxygen bond, as occurs with alkaline metal perchlorates (Boldyrev 2006). According to a third point of view, the thermal decomposition of ammonium perchlorate takes place through a proton transfer mechanism from ammonia cation NH_4^+ to ClO_4^- anion, forming perchloric acid ($HClO_4$) and ammonia (NH_3), which adsorb on ammonium perchlorate surface or desorb and sublime, interacting in the gas phase (Chaturvedi and Dave 2013; Boldyrev 2006).

Generally speaking, the presence of nanocatalysts such as α-Fe_2O_3 alters significantly the transitions of thermal reactions of ammonium perchlorate oxidizer. In fact, the catalytic effect is mainly observed on the high-temperature decomposition region, with changes in the exothermic positions. Thus, kinetic parameters of thermal reactions, such as activation energy and decomposition enthalpies, also exhibited alterations, thus confirming the catalytic effect of nanomaterials (Joshi *et al.* 2008; Boldyrev 2006).

Xu *et al.* (2008) reported the selective synthesis of α-Fe_2O_3 nanorods and micro-octahedrons through one-step hydrothermal reactions. By using differential scanning calorimetry (DSC) technique, they further carried out a comparative study of the catalytic performance of different α-Fe_2O_3 nanorods samples, micro-octahedrons and irregular particles on the thermal decomposition of ammonium perchlorate. Morphology of the resulting samples was investigated through scanning electron microscopy (SEM) – nanorods presented diameters of 120 to 30 nm and lengths of 50 to 100 nm (aspect ratio of 4 to 8) while octahedrons were 100 to 400 nm in size. It was found that all exothermal peaks of AP in the high-temperature region were shifted to lower temperatures, indicating that the different samples of α-Fe_2O_3 can indeed promote the thermal decomposition of ammonium perchlorate. The best catalytic effect of α-Fe_2O_3 nanorods was attributed to its small particle size and more active sites which can enhance the rate of heterogeneous decomposition of deprotonized $HClO_4$ gas on the surface of catalyst particles. On the other hand, the performance of irregular particles resulted slightly better than the micro-octahedron ones, indicating that the shape of the catalyst particles by itself may not affect the catalytic reaction. This study provides an alternative choice for burning rate catalysts for application in composite solid propellants (Xu *et al.* 2008).

Joshi *et al.* (2008), in a comparative study on the catalytic effect of iron oxide (α-Fe_2O_3) on nano and microscale (commercial) hematite in the thermal decomposition reaction of ammonium perchlorate, observed that, due to huge surface area, the nanoscale iron oxide contains many active sites on the surface. Accordingly, these sites adsorb reactive gaseous molecules NO, O_2, Cl_2 and H_2O which are released at low temperature and during the second phase of ammonium perchlorate decomposition, thus promoting the complete decomposition of AP. Compared to nanometal oxide, commercial iron oxide shows lower catalytic effect in high catalytic thermal decomposition region of AP (> 673 K) (Joshi *et al.* 2008).

According to some researchers (Ma *et al.* 2006), the high catalytic effect of iron oxide in the thermal decomposition reactions of NH_4ClO_4 is due to the mechanism of proton transfer. As stated in this mechanism, the formation of perchlorid acid ($HClO_4$) plays a key role in catalytic reactions. The volatile products from thermal decomposition of $HClO_4$ catalyze the combustion of propellant and in consequence iron oxide catalyzes the decomposition of AP. Based on proton transfer theory, the key features for good catalytic performance of iron oxide are: (i) particles of catalyst have high reactivity with AP particles during propellant combustion process; (ii) high specific surface area of iron oxide particles which is coated by the AP and so leads to improved dispersibility and increased interfacial surface area in the mixture (Fe_2O_3/AP) (Ma *et al.* 2006).

Recently, Yuan *et al.* (2014) studied catalytic activity of iron oxide nanoparticles (50 – 80 nm) by using DSC. They concluded that iron oxide has a strong influence on the third stage of thermal decomposition of AP (723 – 753 K) and that the 3d orbit (Fe^{3+}) of Fe_2O_3 has high performance during electron transfer. In gas adsorption and catalytic reactions, the transition metallic oxides (Fe_2O_3) have attracted great interest, due to their redox properties and high specific surface area (Oliveira *et al.* 2013). During the thermal decomposition of a Fe_2O_3/AP mixture, iron oxide receives the electrons which are released from perchlorate ion to ammonium. However, nanoparticles of iron oxide are susceptible to aggregate and expose less active sites to absorb electrons during exothermic reactions of AP (Yuan *et al.* 2014).

Moreover, one of the most important parameters to characterize the performance of composite solid propellants is the burning rate which is function of the internal pression of combustion chamber, usually expressed by the following empirical equation $V = a \times P^n$ (Kubota 2007), where V is the burning rate (mm.s^{-1}), a is an empirical constant, n is the pressure exponent or combustion index and P is chamber pressure of combustion (MPa) (Davenas 1993; Kubota 2007). In general, the burning rate increase of propellant depends on catalysts characteristics, such as chemical composition, crystallinity, size and particle shape.

CHARACTERIZATION

MICROSCOPIC TECHNIQUES

It is known that microscopic techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are widely employed to characterize the crystal structures, for example, morphologies as plates, rods, discs, cubes, ellipsoids, among others. The degree of structural and the crystal size of iron oxide (hematite, magnetite, and maghemite) vary according to methods of preparation (Cornell and Schwertmann 2000).

SEM is a type of versatile electron microscope that, due to its several characteristics, is commonly used to investigate the surface structure (polished or rough) or subsurface sample with relatively large dimensions (Canevarolo Jr 2004; Mannheimer 2002). SEM image has a large depth of field and high resolution, which is easy to interpret (Mannheimer 2002), and it provides a 3-D image (Mannheimer 2002; Cornell and Schwertmann 2000). As a result of the electron beam interaction with the sample surface, a series of radiation are emitted: (i) secondary electrons, which are emitted from the sample atoms with low-energy (typically 50 eV or less); (ii) backscattered electrons (the reflection of images with topography contrast); (iii) X-ray detectors (used for chemical analysis) (Canevarolo Jr 2004). These radiation characteristics provide sample information such as topography of the surface, composition and crystallography.

TEM was built by Max Knoll and Ernest Ruska in 1931 and then this technique has been widely employed in contrast images, the electrons are transmitted or diffracted from a family of well-defined crystal planes (Canevarolo Jr 2004). TEM offers the following information: bright and dark file images, concerning the microstructure and morphology of the sample; X-ray analysis of elemental composition of the sample (Mannheimer 2002). In addition to resolution, the TEM image requires that the sample present contrast (ability to distinguish the crystal structures). Image contrast can be achieved by elastic and inelastic scattering through interaction of the incident primary electron beam with the specimen and is divided into three classes: absorption contrast (sample image forming polycrystalline monophasic) (Mannheimer 2002); diffraction contrast (the scattered electrons can be arranged in the form of spots or rings, according to the Bragg's Law) (Mannheimer 2002; Canevarolo Jr 2004); phase contrast (obtaining of crystalline lattice images, range: 1 nm) (Canevarolo Jr 2004).

SPECTROSCOPIC TECHNIQUES

Different methods can be used to determine size characterization of iron oxide nanoparticles. Spectroscopic techniques provide additional information to identify the chemical composition: (i) X-ray diffraction can be performed to obtain the crystalline structure of particles (angle position, width and intensity). The main details of crystallographic structures of iron oxides (hematite, magnetite, and maghemite) were established in 1915 by Bragg and Nishikawa (Cornell and Schwertmann 2000). From these crystallographic structures, the crystallographic descriptions were established, such as orthorhombic, hexagonal, cubic, octahedral, tetrahedral, and the atomic coordinates of polymorphous iron oxides (Cornell and Schwertmann 2000); (ii) energy dispersive X-ray (EDX) spectroscopy: the X-rays are emitted during the interaction with the electron beam, allowing the determination of chemical elements in the samples. The results are shown as spectra, which consists of a series of peaks representing the type and quantity of each chemical element of samples (Cornell and Schwertmann 2000; Dedavid *et al.* 2007); (iii) Fourier transform infrared spectroscopy (FT-IR) has been used as a technique for the investigation of the characteristic functional groups of iron oxides and characterization of precursors from different synthesis methods.

Infrared (IR) absorption spectroscopy is the measurement of the wavelength or wavenumber and intensity of the absorption of infrared light by a sample. Usually, an infrared spectrum is the result of band transmittance (range: 100 to 0%) versus the frequency of the incident radiation given in wavenumber (range: 4000 to 660 cm^{-1}). In a usual transmission mode, the infrared beam passes through the sample, and the transmittance or absorbance of IR radiation as a function of wavenumber or wavelength is measured (Ryczkowski 2001).

Generally, the main types of iron oxides, hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3), present different spectra of absorption. Even some impurities from synthesis methods of iron oxide have distinct bands: at 1700 cm^{-1} (oxalate); 1400 cm^{-1} (nitrate); 1300 and 1500 cm^{-1} which can be attributed to carbonate. The other important bands are visualized as shoulder at 3720, 3700, 3635, 3490 and 3380 cm^{-1}, corresponding to stretch vibration of hydroxyl groups (OH) (Cornell and Schwertmann 2000).

Hematite in its crystalline form contains no structural OH groups of water in 3400 cm^{-1}, which is a characteristic of aqueous methods or characteristic of FT-IR technique, as a function of absorbed humidity (commonly based on potassium bromide – KBr) during the preparation of pellets (Hummel and School 1981). FT-IR spectrum characteristics of maghemite showed peaks at 3740 and 3725 cm^{-1}; both peaks can be attributed to singly coordinated OH and two strong bands at 3675 and 2640 cm^{-1}, while magnetite (Fe_3O_4) shows spectrum broad peaks at 580 and 400 cm^{-1}.

PHYSICAL ADSORPTION ANALYSIS

In addition to optical and spectroscopic techniques, textural and structural properties are important parameters, particularly when iron oxides are used as catalysts. Textural properties, such as specific surface area, pore size, and shape are highly dependent of its particle characteristics (Cornell and Schwertmann 2000; Sing 1982). In order to obtain the specific surface area of a solid, Brunauer-Emmett-Teller (BET) method is commonly used. This method employs nitrogen gas as adsorbate and liquid nitrogen (77 K) as coolant. The specific surface area is obtained in the relative pressure range P/P_0 between 0.05 and 0.35. Pore size, shape and distributions of pores can be calculated from the desorption branch of the isotherm, with methods based on the Barret, Joyner and Halenda (BJH) (Lowell and Shields 1984).

According to literature, the values of surface area and porosity are dependent on synthesis methods. For example, the hematite synthesized by sol-gel methodology shows the specific surface area (12.4 m^2.g^{-1}); after be calcinated at 1073 – 1173 K, its specific surface area decreases (5 m^2.g^{-1}) due to the sintering process (Cornell and Schwertmann 2000).

Okoli *et al.* (2012) synthesized iron oxide nanoparticles from two different microemulsion: water-dispersed-in-oil (w/o) and oil-dispersed-in-water (o/w) systems. When comparing the two samples of iron oxide, it was observed that the system sample (w/o) presents a smaller specific surface area (147 m^2.g^{-1}) and pore size (18 nm) than that from system (o/w) (pore size: 5 nm; 304 m^2.g^{-1}). These results indicate that microemulsion synthesis parameters, such as the ratio of oil and water and surfactant concentration, directly influence the characteristics of nanometer scale iron oxide catalysts, such as specific surface area and pore size (Okoli *et al.* 2012).

CONCLUSION

The present article briefly presents the characteristics of nanosized metallic iron oxides, as well as their methods of synthesis, main techniques of characterization and also their application in thermal decomposition of AP, thus contributing to researches in composite solid propellants field.

Transition metal oxides at nanoscale as iron oxides, hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) have been widely applied in catalytic reactions as well as on thermal decomposition of ammonium perchlorate. Their catalytic activities are strongly dependent on the size of their particles and surface area. They are more effective than conventional catalysts for two reasons that correlate: quantum effect due to the reduction in size and surface effect. As a result of the reduction of particle size, there is an increase in atoms located on the surface and consequently an increase in the catalytic activity of nanoparticles iron oxide-hematite and maghemite.

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