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Review on Microwave-Assisted Synthesis of Metal-Oxide Nanocomposites

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ABSTRACT

An extensive work for the study of SnO_2 samples doped with x-mol% of Sb (x = 0, 6, 10, 14 and 18) is reported. The materials were prepared by the polymeric precursor method (Pechini method), calcined for 4 hrs between 800 8C and 1200 8C. The Rietveld method with X-ray diffraction data (XRD) was used to analyze the unit cell dimensions, crystallite size and microstrain. The synthesis of tin oxide nanoparticles with high thermal stability against particle growth rate was achieved by doping SnO_2 particles with Sb_2O_3. All the phases tend to have the same dimension when the temperature increases, although its values vary with x and reaches the maximum value when fired at 1100 °C. These variations seem to be an indication that the oxidation state of the antimony changes with the amount of Sb added to the material. © 2008 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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INTRODUCTION

The use of microwave irradiation as an alternative heat source is becoming more and more popular in chemistry. Its good acceptance in inorganic and organic synthesis arises from the immense increase in reaction speed, which compares favourably with conventional heating for a large number of reactions. Apart from this main advantage, significant improvements in yield, reduction of side reactions and cleaner products have been observed. A simple explanation of the above phenomena is the different mechanism of heating. Traditionally, chemical synthesis has been achieved through conductive heating with an external heat source. Heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and reactants.

This is a slow and inefficient method for transferring energy into the system because it depends on the thermal conductivity of the various materials that must be penetrated. The thermal equilibrium between the temperature of the vessel and the reaction mixture can take hours (Hoogenboom & Schubert, 2007; Sinnwell and Ritter, 2007; Chauveau *et al*., 2008**).**

The technological advancements in the field of petrochemical-based polymers have brought many benefits to mankind. However, it is also becoming more and more evident that the ecosystem has been considerably disturbed and damaged as a result of the extensive use of non- degradable petro-plastics. The environmental impact of plastic wastes is causing global concerns as their disposal methods are limited. Incineration of the plastic wastes produces a large amount of carbon dioxide and other toxic gases, which contribute to global warming as well as and pose serious health risks. On the other hand, satisfactory landfill sites are also limited. Thus, there is an urgent need to develop renewable resource-based environmentally benign biodegradable plastic materials, especially for short-term packaging and other disposable applications that would not involve the use of toxic components in their manufacture and would facilitate composting with the naturally occurring biodegradable products.

Degradable plastics, as defined by the American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO), are those which can go through a significant change in the chemical structure under specific environmental conditions (Kolybaba *et al*., 2003). Biodegradable plastics get degraded with the help of naturally occurring microorganisms such as bacteria and fungi. The main attraction of these polymers is their biodegradation and mineralization to benign end-products after the use of the main product by consumers and their disposal into the bio-waste collection system for composting. This whole process will finally leave behind only CO_2 and H_2O as final products.

There are two broad types of biodegradable polymers natural and synthetic. Natural polymers include polysaccharides (starch, cellulose), proteins (gelatine, wool, silk), lipid fats (fats and oil), polyesters produced by plants or microorganisms [poly(hydroxyalkanoates) PHAs], polyesters derived from bio-derived monomers [poly(lactic acid) PLA], and several miscellaneous polymers like natural rubber and composites. The second group includes non-renewable petroleum based synthetic, and biodegradable plastics such as poly(butylene succinate) (PBS) and poly(caprolactone) (PCL). There are some biodegradable polymers which do not come into either category. These are poly anhydrides and poly vinyl alcohol. The most widely studied biodegradable polymers which are likely to be the most promising replacement for petrochemical based thermoplastic are polyesters. In recent years, the application of such biodegradable aliphatic polyesters has got a boost with their increasing use in everyday use materials and medical and health care devices.

Microwave-assisted chemical synthesis has been known since 1986. The first results of microwave irradiation in chemical synthesis were published in 1986 [Giguere *et al.* (1986); Gedye *et al.* (1986)]. The use of microwave for synthesis of inorganic solid is a very efficient and useful technique in material chemistry. The microwave has been used in preparation of ceramics and theoretical modeling of microwave interaction with ceramic materials have been studied by Ayappa *et al.* (1997); Kenkre *et al.* (1991); Lee *et al.* (1997); Rao *et al.* (1994). They reported that when Si and C (Charcoal) in their powder form are taken in silica crucible and is exposed to microwave for 4 to 10 min in a domestic microwave oven operating at 2.45 GHz, SiC is obtained [Ramesh *et al.* (1994)]. SiC is a large volume ceramic material and is extensively used for industrial application such as for grinding wheels and in the manufacture of abrasion tools. Microwave technology in nanoscience [Pileni *et al.* (1997); He *et al.* (1999)] is being applied in the fields of synthesis of single-site catalyst, antimicrobial nanocomposites, fire retardant materials, novel electro-optical devices, sensors, ultra-soft magnets and also in the area of drug delivery systems [Larhed and Hallberg (2001)]. The application of microwave irradiation in the field of analytical chemistry includes sample digestion and solvent extraction techniques [Camel (2000); Wang *et al.* (2007)]. Development of high pressure asher focused microwave, a novel approach to microwave digestion, is described by Matusiewics *et al.* (1999). The system uses focused MW operating at 2.45 GHz at 650 W power. Using this apparatus the methodology was developed for digestion of biological reference material such as bovine liver.

Application of MW in polymer synthesis has been known for the past ten years. Microwave- assisted polymer synthesis was used in radical polymerizations, step-growth polymerizations,ring-opening polymerizations, and polymer modifications. The MW-assisted radical crosslinking of unsaturated polyester with styrene was reported first by Gourdenne *et al.* (1979). Extensive reviews on microwave-assisted polymer synthesis presented by Sinnwell and Ritter (2007); Zhang *et al.* (2007) focus on ring opening polymerization and Kempe *et al.* (2011). The synthesis of polyacrylamide (PAM) was studied under microwave irradiation [Li *et al.* (1992)]. The use of microwave in the synthesis of biodegradable polymers has attracted the attention of researchers during the last few years. The examples are polycaprolactone (PCL) [Kappe and Stadler (2006)], and polylactic acid (PLA). PCL has been synthesized by ROP of caprolactone with $Sn(Oct)_2$ as a catalyst, which has been approved by FDA as a food additive.

LITERATURE REVIEW

The crystallization of blends of two semi-crystalline polymers nylon-11 and poly(vinylidene fluoride) was studied. The existence of separate melting and crystallization temperatures over the whole composition range showed that these two polymers did not co-crystallize. However, blending affected the crystallization behavior of each component. Adding nylon-11 decreased the crystallization temperature (T_c) of poly(vinylidene fluoride), but increased its crystallization rate. On the other hand, the T_c of nylon-11 decreased, and its crystallization rate decreased as well when blended with PVF_2. The crystallization mechanism of both nylon-11 and PVF_2 changed in the blends compared to that in the pure states. The Ozawa index, or Avrami exponent, of poly(vinylidene fluoride) in the blend decreased from 3 to 1 as the crystallization temperature decreased from 137°C to 131°C, compared with a decrease from 2.5 to 1.3 observed in pure PVF_2 at the temperature range from 145 °C to 135 °C. The Avrami exponent of nylon-11 in the blend decreased from 2 to 1 as the crystallization temperature decreased from 159 °C to 153 °C, compared with a decrease from 2.5 to 0.75 observed in pure nylon-11 at the same temperature range (Gao and Scheinbeim, 2023).

Various (meth) acrylamides were synthesized in good yields directly from (meth) acrylic acid and an amine using microwave irradiation in a solvent-free environment. Under the applied conditions the (meth)acrylic function is preserved. Furthermore, the addition of an initiator like AIBN to the starting mixture leads directly to poly(meth)acrylamides in a single step (Goretzki *et* al., 2021).

The crystallization behavior of poly(ethylene terephthalate) (PET)/poly(ethylene- 2,6-naphthalate) (PEN) blends before and after microwave irradiation for different time intervals has been investigated by means of WAXD and DSC techniques. It was found that microwave irradiation could greatly affect the crystallization behavior of PET/PEN blends and significantly enhance their degree of crystallinity. For the PET/PEN (90/10) blends, the degree of crystallinity increased from 15 to 45% and for the PET/PEN (60/40) blends, the degree of crystallinity significantly increased, from 1 to 36%. However, with increasing irradiation time, the degree of crystallinity didn't continually increase. It reached a maximum at certain time point. The cold crystallization enthalpy Δ Hcc gradually decreased as microwave irradiation time increased and the melting enthalpy Δ Hm Vis-ả-Vis the long time interval of such irradiation was decreased. In addition, the mechanism for microwave irradiation affecting the crystallization behavior of polymers is discussed (Li *et* al., 2020).

MICROWAVE SYNTHESIS AND MEDICINAL CHEMISTRY

Improving research and development (R&D) productivity is one of the biggest tasks facing the pharmaceutical industry. In the next 10 years, the pharmaceutical industry will see many patents of drugs expire. In order to remain competitive, pharma companies need to pursue strategies that will offset the sales decline and see robust growth and shareholder value. The impact of genomics and proteomics is creating an explosion in the number of drug targets. Today’s drug therapies are based solely on approximately 500 biological targets, while in 10 years from now the number of targets could well reach 10000. In order to identify more potential drug candidates for all of these targets, pharmaceutical companies have made major investments in high-throughput technologies for genomic and proteomic research, combinatorial chemistry, and biological screening. However, lead compound optimization and medicinal chemistry remain the bottlenecks in the drug discovery process. Developing chemical compounds with the desired biological properties is time-consuming and expensive. Consequently, increasing interest is being directed toward technologies that allow more rapid synthesis and screening of chemical substances to identify compounds with functional qualities.

Medicinal chemistry has benefited tremendously from the technological advances in the field of combinatorial chemistry and high-throughput synthesis. This discipline has been the innovative machine for the development of methods and technologies which accelerate the design, synthesis, purification, and analysis of compound libraries. These new tools have had a significant impact on both lead identification and lead optimization in the pharmaceutical industry. Large compound libraries can now be designed and synthesized to provide valuable leads for new therapeutic targets. Once a chemist has developed a suitable high-speed synthesis of a lead, it is now possible to synthesize and purify hundreds of molecules in parallel to discover new leads and/or to derive structure–activity relationships (SAR) in unprecedented timeframes.

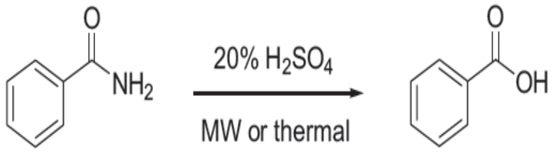
The bottleneck of conventional parallel/combinatorial synthesis is typically optimization of reaction conditions to afford the desired products in suitable yields and purities. Since many reaction sequences require at least one or more heating steps for extended time periods, these optimizations are often difficult and time-consuming. Microwave-assisted heating under controlled conditions has been shown to be an invaluable technology for medicinal chemistry and drug discovery applications since it often dramatically reduces reaction times, typically from days or hours to minutes or even seconds. Many reaction parameters can be evaluated in a few hours to optimize the desired chemistry. Compound libraries can then be rapidly synthesized in either a parallel or (automated) sequential format using this new, enabling technology. In addition, microwave synthesis allows for the discovery of novel reaction pathways, which serve to expand “chemical space” in general, and “biologically relevant, medicinal chemistry space” in particular.

Specifically, microwave synthesis has the potential to impact upon medicinal chemistry efforts in at least three major phases of the drug discovery process: lead generation, hit-to-lead efforts, and lead optimization. Medicinal chemistry addresses what are fundamentally biological and clinical problems. Focusing first on the preparation of suitable molecular tools for mechanistic validation, efforts ultimately turn to the optimization of biochemical, pharmacokinetic, pharmacological, clinical, and competitive properties of drug candidates. A common theme throughout this drug discovery and development process is speed. Speed equals competitive advantage, more efficient use of expensive and limited resources, faster exploration of structure– activity relationships (SAR), enhanced delineation of intellectual property, more timely delivery of critically needed medicines, and can ultimately determine positioning in the marketplace. To the pharmaceutical industry and the medicinal chemist, time truly does equal money, and microwave chemistry has become a central tool in this fast-paced, time-sensitive field.

Chemistry, like all sciences, consists of never-ending iterations of hypotheses and experiments, with results guiding the progress and development of projects. The short reaction times provided by microwave synthesis make it ideal for rapid reaction scouting and optimization, allowing very rapid progress through the “hypotheses- experiment-results” iterations, resulting in more decision points per unit time. In order to fully benefit from microwave synthesis, one has to “be prepared to fail in order to succeed”. While failure could cost a few minutes, success would gain many hours or even days. The speed at which multiple variations of reaction conditions can be performed allows a morning discussion of “What should we try?” to become an after lunch discussion of “What were the results?” (the “let’s talk after lunch” mantra) [1]. Not surprisingly, therefore, most pharmaceutical, agrochemical, and biotechnology companies are already heavily using microwave synthesis as frontline methodology in their chemistry programs, both for library synthesis and for lead optimization, as they realize the ability of this enabling technology to speed chemical reactions and therefore the drug discovery process.

Microwave-Assisted Organic Synthesis (MAOS) – A Brief History

While fire is now rarely used in synthetic chemistry, it was not until Robert Bunsen invented the burner in 1855 that the energy from this heat source could be applied to a reaction vessel in a focused manner. The Bunsen burner was later superseded by the isomantle, the oil bath or the hot plate as a means of applying heat to a chemical reaction. In the past few years, heating and driving chemical reactions by microwave energy has been an increasingly popular theme in the scientific community [1,2]. Microwave energy, originally applied for heating foodstuffs by Percy Spencer in the 1940s, has found a variety of technical applications in the chemical and related industries since the 1950s, in particular in the food-processing, drying, and polymer industries. Other applications range from analytical chemistry (microwave digestion, ashing, extraction) [3] to biochemistry (protein hydrolysis, sterilization) [3], pathology (histoprocessing, tissue fixation) [4], and medical treatments (diathermy) [5]. Somewhat surprisingly microwave heating has only been implemented inorganic synthesis since the mid-1980s. The first reports on the use of microwave heating to accelerate organic chemical transformations (MAOS) were published by the groups of Richard Gedye (Scheme 1.1) [6] and Raymond J. Giguere/George Majetich [7] in 1986. In those early days, experiments were typically carried out in sealed Teflon or glass vessels in a domestic household microwave oven without any temperature or pressure measurements. The results were often violent explosions due to the rapid uncontrolled heating of organic solvents under closed-vessel conditions. In the 1990s, several groups started to experiment with solvent-free microwave chemistry (so-called dry-media reactions), which eliminated the danger of explosions [8]. Here, the reagents were pre-adsorbed onto either an essentially microwave-transparent (i.e., silica, alumina or clay) or strongly absorbing (i.e., graphite) inorganic support, that additionally may have been doped with a catalyst or reagent. Particularly in the early days of MAOS, the solvent-free approach was very popular since it allowed the safe use of domestic microwave ovens and standard open-vessel technology. While a large number of interesting transformations using “dry-media” reactions have been published in the literature [8], technical difficulties relating to non-uniform heating, mixing, and the precise determination of the reaction temperature remained unresolved, in particular when scale-up issues needed to be addressed.



Thermal: 1 h, 90 % yield (reflux)
MW: 10 min, 99 % yield (sealed vessel)
Scheme 2.1 Hydrolysis of benzamide. The first published example (1986) of microwave-assisted organic synthesis.

Alternatively, microwave-assisted synthesis has been carried out using standard organic solvents under open-vessel conditions. If solvents are heated by microwave irradiation at atmospheric pressure in an open vessel, the boiling point of the solvent typically limits the reaction temperature that can be achieved. In order to nonetheless achieve high reaction rates, high-boiling microwave-absorbing solvents have been frequently used in open-vessel microwave synthesis [9]. However, the use of these solvents presented serious challenges in relation to product isolation and recycling of the solvent. Because of the recent availability of modern microwave reactors with on-line monitoring of both temperature and pressure, MAOS in dedicated sealed vessels using standard solvents – a technique pioneered by Christopher R. Strauss in the mid-1990s [10] – has been celebrating a comeback in recent years. This is clearly evident surveying the recently published (since 2001) literature in the area of controlled microwave-assisted organic synthesis (MAOS). It appears that the combination of rapid heating by microwaves with sealed-vessel (autoclave) technology will most likely be the method of choice for performing MAOS on a laboratory scale in the future. Importantly, recent innovations in microwave reactor technology now allow controlled parallel and automated sequential processing under sealed-vessel conditions, and the use of continuous- or stop-flow reactors for scale-up purposes.

Since the early days of microwave synthesis, the observed rate accelerations and sometimes altered product distributions compared to oil-bath experiments have led to speculation on the existence of so-called “specific” or “non-thermal” microwave effects [11]. Historically, such effects were claimed when the outcome of a synthesis performed under microwave conditions was different from that of the conventionally heated counterpart at the same apparent temperature. Reviewing the present literature [12], it appears that today most scientists agree that in the majority of cases the reason for the observed rate enhancements is a purely thermal/kinetic effect, i.e.,a consequence of the high reaction temperatures that can rapidly be attained when irradiating polar materials in a microwave field,although effects that are caused by the unique nature of the microwave dielectric heating mechanism (“specific microwave effects”) clearly also need to be considered. While for the medicinal chemist in industry this discussion may seem largely irrelevant, the debate on “microwave effects” is undoubtedly going to continue for many years in the academic world. Regardless of the nature of the observed rate enhancements (for further details on microwave effects, see Section 2.5), microwave synthesis has now truly matured and has moved from a laboratory curiosity in the late 1980s to an established technique in organic synthesis, heavily used in both academia and industry.

The initial slow uptake of the technology in the late 1980s and 1990s has been attributed to its lack of controllability and reproducibility, coupled with a general lack of understanding of the basics of microwave dielectric heating. The risks associated with the flammability of organic solvents in a microwave field and the lack of available dedicated microwave reactors allowing for adequate temperature and pressure control were major concerns. Important instrument innovation now allows for careful control of time, temperature, and pressure profiles, paving the way for reproducible protocol development, scale-up, and transfer from laboratory to laboratory and from scientist to scientist. Today, microwave chemistry is as reliable as the vast arsenal of synthetic methods that preceded it. Since 2001, therefore, the number of publications related to MAOS has increased dramatically.

MICROWAVE CHEMICAL SYNTHESIS

Previous research has revealed several advantages from microwave-assisted wet chemical synthesis in reaction acceleration, yield improvement, enhanced physicochemical properties and the evolvement of new material phases. The study present examples that demonstrate the significance of these advantages to industrial application. In order to achieve successful industrial application there is a need to distinguish between the microwave athermal (not excited by heat) effects from the microwave-induced thermal effect (temperature rise). The optimization of this new process has to be systematically investigated, so the advantages and benefits of this new technology can be fully exploited.

Advantages and significance of Fe_2O_3 based magnetic materials

Fe_2O_3 based magnetic materials have been extensively used as recording materials because of their good magnetic properties. The emergence of nanomagnetic technology has imposed new demands upon magnetic materials. To fabricate ultrahigh density and ultrahigh speed data storage devices, which work on the magnetic -spintronic concept, magnetic materials with nanoscale particles are highly preferred [1].

Conventionally, Fe_2O_3 powders with monodispersed particles are synthesized first by means of forced hydrolysis of ferric nitrate or ferric chloride in aqueous solutions, which produces a Fe_2O_3, and then the a- Fe_2O_3 are transformed into Fe_2O_3 in a high-temperature process [2], [3]. To effectively control the particle shape and particle size, which are essential for achieving the desired magnetic properties, the hydrolysis solution must be very dilute. For producing micron- and submicron-sized particles, the concentrations of the ferric irons are generally within a range around 0.02M [2], [4], [5] and for producing nanosized powders, the ferric concentration should be much lower. In addition to dilute solutions, the conventional hydrolysis has to be carefully controlled and it generally requires 2-7 days. This means that, even based upon the shortest processing time and highest concentration, the rate for producing the nanosized iron oxide powders would be less than 0.014 gram per liter per hour. In order to use nanosized magnetic materials for industrial applications, appreciable acceleration of the process and an increase in the ferric concentration are required.

Several researchers have attempted the iron oxide synthesis via microwave-assisted hydrolysis. Komarneni et al demonstrated that under otherwise identical processing conditions, synthesis of crystalline hematite by a microwave-hydrothermal approach was 36 times faster than by conventional hydrothermal methods [6]. Our study shows the capability of controlling the particle shape and particle size with this rapid synthesis approach. Rigneau et al further shortened the processing time to 30 minutes and also increase the ferric concentration to 0.05M [7], which could increase the production rate over one hundred times. The even more striking finding from their results was that the microwave synthesized Fe_2O_3 particles were nano scale and directly type. The significance of this finding is that it could not only remarkably simplify the synthesis procedure, but also get rid of the difficulties involved with the calcination of nano powders, and avoid the detrimental microstructure changes that accompany the transformation from a- Fe_2O_3 to ?- Fe_2O_3 in the conventional high temperature process.

Insertion electrode materials

The role of intercalation/insertion reactions in battery electrodes was first recognized about 30 years ago. From the first prototype titanium disulfide cells, the technology has more recently been commercialized in Li-ion cells using a cobalt oxide insertion cathode and a carbon insertion anode. This technology has proven highly successful in small devices. Since the conduction species intercalated in the structure exhibit very good electrical conductivity, insertion electrode materials are also considered most promising in large device and large-scale applications [8].

The extensive research and development on new insertion materials can be recognized from Whittinghan’s Work. His investigation has covered a diverse group of layered and intercalated compounds including titanium disulfide [9], [10], lithium cobalt oxide [11], tetramethylammonium intercalated vanadium oxides [12], layered-structure manganese dioxides [13] and vanadium-pillared manganese oxide structures [14]. More recently, the group is investigating vanadium oxide nanotubes, which is considered to have significant advantages due to its distinct electrical contact regions and electrolyte-filled channels [15].

The insertion materials are normally synthesized via conventional hydrothermal method. The synthesis is a tedious procedure and often takes several days to a week. The use of the microwave method has been attempted to accelerate the synthesis of layered vanadium oxide inserted with tetramethylammonium ions [12]. It was found that this method could reduce the synthesis time to minutes and also found that longer microwave hydrothermal treatment could lead to a new material structure. The adoption of the microwave method to the insertion material synthesis could not only develop a highly efficient, low cost process for synthesis of insertion materials synthesis, but also offer chances to generate new material structures that could not be obtained from conventional methods.

Molecular sieves

Crystalline molecular sieves have intraframework cages and channels of uniform microporous or mesoporous size, tailor-made acidity or basicity, and high thermal stability. Owing to these unique structures, the materials have acquired various applications in the petroleum refining and petrochemical industry [16]. The advent of nanotechnology has provided a new field for their application. The materials can be used as a high performance nanostrucutured host for preparation of advanced materials that exhibit specific optic, optoelectronic, and electrochemical properties suitable for molecular wire, quantum electronics and non-linear optical devices. A number of preparations of nanoscale materials on such a nanostructured template have been demonstrated including the synthesis of organized metal clusters, metal oxides or sulfides, isolated conducting polymers as well as confined supermolecular compounds [17-30].

The structure of the molecular sieve frameworks is of great diversity. It is sensitive to synthesis conditions. Generally, it takes several days to several weeks for obtaining the desired material. Raising the temperature may shorten the synthesis time but could result in different structures. There are often several structures concurrently in development. Although each structure may have a dominating stage, the product is more liable to mixed structures31. The process is often complicated and time-consuming for synthesizing a pure product with tailored structure.

Microwave-assisted synthesis has been attempted on a certain type of molecular sieves. Significant kinetic acceleration has been demonstrated in synthesis of MgAPO-5 (20min microwave vs 24h conventional) by Cresswell et al [32] and in synthesis of MCM-41 (4h microwave vs 7-14d conventional) by U. Oberhagemann et al [33]. The microwave method is also produces high surface area structures. While multi-point surface area of the conventional synthesized MgAPO-5 is only 4.48 m2g-1, that of the microwave synthesized MgAPO-5 attains 34.97 m2g-1, about 7 times surface enlargement. The microwave method further shows its effectiveness in producing pure structures, as were the cases for the synthesis of AlPO4-11 and the synthesis of cloverite (Park et al34). In these instances, the microwave method was able to obtain these pure crystalline phases in 2.5h and 2.7h respectively, whereas over 1-day conventional preparation produced AlPO4-11 mixed with some amount of AlPO4-31 and a trace of AlPO-tridymite or produced cloverite with unreacted reactants. Further advantage of the microwave approach was found in the ease of processing stage control. Carmona et al [35] investigated the microwave-assisted synthesis of VPI-5 along with conventional approaches. With microwave-activated refluxing method, pure VPI-5 was the only product of the process. With other methods, however, several phases appeared as the processing proceeded.

Organometallic compounds

Organometallic compounds are generally defined as having a metal-carbon bond with properties distinct from those of inorganic compounds. Orgaometallic compounds cover a large number of varieties, which contain many kinds of metal elements. Some groups have high reactivity and reaction selectivity and are used as various kinds of catalysts or as organosynthetic reagents. Others have chemical stability and have acquired their applications in microbiocides, pesticides, anticancer agents, water repellants, octane number improvement, and antifoaming and mold releasing. Organometallic compounds are also employed as precursors for preparing ultrahigh purity metals and functional ceramics with tailored compositions and structures, such as semiconductor elements, electroconductive materials, magnetic materials, hard materials, heatresistant materials and superconductive materials, etc36.

Preparation of organometallic compounds involves reactions of metal elements, metal salts or other organometallic intermediates with inorganic compounds, gases or organic reagents 37. The synthesis rate varies considerably, with a few that are within one hour 38 but a number of others require several hours or even days [39].

The microwave-enhanced kinetics in synthesis of organometallic compounds was reported by Gedye et al [40] in 1991, when they synthesized $(C_6H_5)_3SnCl$ and $(C_6H_5)_3SnOH$ in sealed vessels under microwave radiation in 7 and 4 minutes respectively, whereas with conventional reflux method, the synthesis times were correspondingly 3 hours and 1 hour. Laurent et al [41] reported microwave-assisted synthesis of alkyl- or arylhalogermanes by means of Redistribution Reactions. With $AlCl_3$ as the catalyst, Bu3GeCl was synthesized in an open reactor in 85% yield in 3 minutes. The kinetic enhancement was remarkable compared to conventional synthesis that requires 5 hours at 200°C. Vanatta et al [42] studied the application of microwave method to the synthesis of Group 6 (Cr, Mo, W) zerovalent organometallic carbonyl compounds. A rate enhancement of up to two orders of magnitude and a higher yield of microwave-assisted synthesis were achieved compared to conventional reflux method.

	Microwave vs reflux			
Compound	Time (min)	Temp (°C)	Yield (%)	Rate enhancement
(dppe=)Mo(CO)4	0.5/25#	180/120	80/68	50

(dppe=)Mo(CO)4	2/180	180/155	64/55	90
(bipyQ)Mo(CO)4	0.5/90	180/110	99/88	180
(dppe)Cr(CO)4	0.5/135	180/135	86/41	270
(dppm^2)W(CO)4	5/2880	180/165	62/51	576

Table 1. Synthesis of Group 6 (Cr, Mo, W) zerovalent organometallic carbonyl compounds:
synthesis method: microwave / reflux = bis(diphenylphosphino)ethane
Q 2,2'-bipyridine ^{2}bis(diphenylphosphino)methane

Polymers

Poly(e-caprolactam) is an important engineering thermoplastic with a combination of useful thermal and mechanical properties. Its synthetic fiber is widely used and has a global production of more than 3.3 million metric tons. A commercial route to manufacture the polymer is hydrolytic polymerization, which is conventionally carried out in a high pressure reactor at 250- 270°C for about 12-24 h. Fang et al [43] synthesized Poly(e-caprolactam) by means of microwave assisted polymerization in nitrogen at atmospheric pressure. At 250°C for only 2 h, the synthesis was completed with yield, purity, yield strength and tensile strength comparable to the commercial product.

Poly(e-caprolactone) is one of the industrial biopolymers that is used as degradable biomedical and packaging material. It is generally prepared from catalyzed ring-opening polymerization of e-caprolactone in bulk or solution. Although many efforts have been made to catalyze the process, it still takes over 10 h or several days to get the polymerization completed. Liao et al [44] attempted the microwave-assisted ring-opening polymerization of e-caprolactone in sealed ampoules. Using 0.1% (mol/mol) stannous octanoate as catalyst, they synthesized the polymer at 180°C in 30 min. The yield attained 90% and the average molar mass is 124000g/mol.

CONCLUSIONS

The increase of the unit cell is due to the substitution of Sn^{4+} by Sb^{3+} in the SnO_2 lattice. Sb^{3+} and Sb^{5+} coexist at higher concentration of antimony for the materials heated above 900 8C, causing the stability of crystallite size and microstrain. For the material prepared at 800 8C, the amount of Sb^{5+} increase with the addition of antimony. The HRTEM analysis showed that the undoped material is more densely agglomerated than the doped material. These results clearly show that doped antimony can be used to control particle size and stabilize SnO_2 against particle growth at high temperatures.

Heat-bodying (HB) and microwave irradiation (MI) increased the viscosity of soybean oil. Pressurized differential scanning calorimetry showed that the HB considerably improved oxidative stability over the untreated soybean oil, and oil exposed to MI had greater oxidative stability than HB. The most noteworthy finding of this studywas that HB, and to a greater extent MI, lowered the pour point considerably compared with untreated soybean oil despite having an increase in viscosity. ^{1}HNMR analysis showed no occurrence of oxidation regardless of treatment and that the pour point anomaly is most likely the result of the formation of triacylglyceride cyclic ring structures that caused an increase in viscosity. Greater friction was observed for oils treated by HB and MI than the untreated and particularly MI, which left greater wear scratches on the ball and disk surfaces used for lubricity studies. Microwave irradiation shows promise to improve the cold-flow behavior of soybean oil, butMI treatment will not produce superior vegetable oil-based lubricants.

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