

APPLICATION OF MICROWAVE TECHNOLOGY IN RARE EARTH ELEMENTS – A SHORT INQUIRY

Liliane Landini, Sumair G. de Araújo and Ademar B. Lugão

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
llandini@ipen.br
sgaraujo@ipen.br
ablugao@ipen.br

ABSTRACT

In the electromagnetic spectrum, the microwave radiation is located between infrared radiation and radio waves. The frequencies for industrial and scientific purposes are imposed by international convention being the 2.45GHz (wavelength of 12.2cm) the most routinely used. These kind of waves are used for selective heating of materials, whose molecular structures can be affected, depending on their dielectric properties. This phenomenon can be used for some purposes. In materials of multiple phases, some of these can syntonize more readily with these electromagnetic waves. Therefore, it is possible to process materials selectively with distinct phases of heating and to initiate chemical reactions in several composites. In this way, new materials have been developed and studied, such as, the rare earth elements (REEs). They can be used as catalysts, increasing the speed of the reactions in several chemical compounds. The objective of this work was to carry out a short literature inquiry, related to the application of this methodology, using some elements of this family, for heating of materials, as the organic ones. A great improvement of microwave application has been attained, but these processes or technologies still need further researches.

1. INTRODUCTION

In the last decades, microwave heating has been applied in several areas as a very effective and non-polluting method of activation. Examples of this technology are materials processing, industrial and commercial applications, chemistry and biochemistry, among others. In the electromagnetic spectrum, the microwave radiation is located between infrared radiation and radio waves. The wavelengths are between 1mm and 1m with corresponding frequencies in the range of 300MHz to 300GHz. Besides telecommunication and microwave radar equipments occupy many of the band frequencies in this region, most routinely used, for industrial and scientific purposes are imposed by international convention be the 2.45GHz (wavelength of 12.2cm). [1]

Microwave is a relatively new technology alternative for materials processing that provides new approaches for enhancing the material properties as well as economic advantages through energy saving and acceleration of product development. Clearly, advantages in

utilizing this technology include penetration radiation, controlled electric field distributions, rapid heating, self-limiting reactions and selective and volumetric heating. [2]

Depending on the response to microwave heating, materials can be classified into three principal groups with respect to their interaction with a microwave field: transparent or low loss materials where microwaves pass through them without any losses; conductors which reflect microwaves without any penetration; absorbing or high loss materials, which absorb microwaves and dissipate the electromagnetic energy as heat, depending on the value of the dielectric loss factor. Microwave heating of dielectric materials lies in the ability of the electric field to polarize the charge of the material where polarization cannot follow the rapid change of the electric field. [3]

Microwave heating offers several potential advantages over conventional heating for inducing or enhancing chemical reactions. These include direct microwave interaction with certain classes of molecules, volumetric heating rather than heat flow through the vessel wall, less waste heat, increased control over heating rates and the possibility of selective enhancement of desired reactions. This is particularly attractive in the case of catalytic reactions, where it may be possible to selectively promote desirable reactions while suppressing undesirable ones. Also, as a quick, simple and energy efficient method, microwave synthesis has been developed and is widely used for the synthesis of zeolites and ceramic materials. Compared with conventional methods, microwave synthesis has the advantages of very short reaction times, production of small particles with a narrow particle size distribution and high purity. These conveniences could be attributed to fast homogeneous nucleation and ready dissolution of the gel. Unfortunately the exact nature of the interaction of the microwaves with the reactants during the synthesis of materials is somewhat uncertain and speculative. However, it is well known that the interaction between dielectric materials, liquids or solids, and the microwaves leads to what is generally known as dielectric heating in which electric dipoles in such materials respond to the applied electric field. In liquids, this constant reorientation leads to a friction between the molecules, which subsequently generates heat. Many microwave phenomena are poorly understood such as non-thermal effects and the superheating effect.[4]

Some materials have been developed and studied, such as, the rare earth elements (REEs) to initiate chemical reactions in diverse composites, by using microwave technology. The rare earths are a relatively abundant group of 17 elements composed of scandium, yttrium and the lanthanides. The lanthanides are a group of 15 chemically similar elements with atomic numbers 57 through 71, included. Although not a lanthanide, yttrium, atomic number 39, is included in the rare earths because it often occurs with them in nature, having similar chemical properties. Scandium, atomic number 21, is also included in the group, although it typically occurs in rare earths ores only in minor amounts because of its smaller atomic and ionic size. They are relatively abundant in the Earth's crust and world resources are contained primarily in bastnäsite and monazite. Bastnäsite deposits in China and the United States constitute the largest percentage of the world's rare earth economic resources, while monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand and the United States constitute the second largest segment. [5]

The concept of using microwave as an energy source for chemical reactions involving solid

catalysts has been investigated intensively in recent years. These studies show that in some cases the reaction rates are enhanced while in others the product selectivity changes when microwave radiation is used instead of conventional heating. [6] As a heating method, this type of electromagnetic wave plays an important role in materials processing such as rare earths. Their number of publications is increasing rapidly and in this work is made a short inquiry of some developments of microwave applications in this area.

2. LITERATURE REVIEW

Liao et al., in 2001, performed the preparation of monodispersed nanocrystalline CeO₂ powders by microwave irradiation. Ceria (CeO₂) is a rare earth oxide with a high refractive index and a very sharp fundamental absorption edge and is also a highly efficient ultraviolet (UV) absorber (used as an additive to glass) to protect light-sensitive materials, as a coating for corrosion protection of metals, as an oxidation catalyst, and as a counter electrode for electrochromic devices. The preparation of nanocrystalline CeO₂ is very difficult using conventional conditions and in this study, a novel method for the preparation of ultrafine nanocrystalline cerium oxide was reported. Monodispersed nanocrystalline CeO₂ powders were prepared by microwave irradiation by means of hydrolysis of (NH₄)₂Ce(NO₃)₆ in an aqueous solution containing poly(ethylene glycol)-2000 (PEG) and NaAc. The advantage of this process is that it is fast, simple and energy efficient. It is predicted that scaling up of the process may lead to large quantities of nanosized CeO₂ crystallites. It also represents a general method to obtain other oxide nanocrystals.[7]

Lu et al., in 2003, described a single microwave extraction procedure that was conducted to investigate the bioavailability of rare earth elements (REEs) by using different extractants of 0.05 M EDTA, 0.10 M CH₃COOH, 0.10 M HCl, and 0.05 M CaCl₂. The experimental conditions of heating time and microwave power were optimized. A microwave power of 60% and extraction time of 30min were adopted. Compared to the conventional single extraction schemes reported in the literature, the recommended technique shortened the operational time, simplified the experimental task, improved the precision, and obtained consistent results with those obtained by using the conventional methods. In addition, the suggested microwave extraction method has been successfully used to evaluate the bioavailability of REEs in soils. Soil samples collected from 15 sites in China were extracted by four different extractants with microwave ancillary. Extractable REEs from soils were well correlated with REEs contents in shoots of wheat under the greenhouse conditions. [8]

Gopalakrishnan et al., in 2006, studied the effects of microwave radiation on one-step oxidation of benzene to phenol with nitrous oxide over Fe-ZSM-5 catalyst. Direct oxidation of benzene to phenol over Fe-ZSM-5 catalyst was chosen as a model reaction to characterize the influence of microwave irradiation on adsorption-desorption processes during heterogeneously catalyzed reactions. The direct oxidation of benzene was investigated under different reaction conditions (temperature, residence time, reactant-concentrations) and microwave power in a specially designed reactor. The results obtained by additional microwave radiation were compared to those obtained by conventional heating under similar reaction conditions. In addition, ex situ TG-MS analyses were also

conducted to study the sorption behavior. Extensive investigations were carried out to determine adsorption–desorption effects (benzene, phenol and a mixture of both) and the coking behaviour under microwave conditions. Microwave induces a trend towards increased phenol selectivity and relative deactivation during the reaction. However, there was no conclusive improvement in the performance was obtained by means of microwave heating. Fe-form of zeolite ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 92$) was used as catalyst throughout this work. This Fe-ZSM-5 catalyst contained 1.16 wt.% of Fe. The catalyst powder was calcinated at 900°C . The catalyst powder was pressed into pellets before being crushed and sieved to obtain a particle size of 1–1.2mm. One gram of catalyst was diluted with 20ml of quartz glass beads (0.8–1.0mm particle size) and filled in the reactor. Preliminary heat up experiments showed that this catalyst and quartz mixture is transparent to microwave radiation and it will not be heated by microwave. [6]

Ishak and Daud, in 2006, designed a simple microwave heating system for firing phosphor samples. An 800W magnetron operating at 2.45GHz was used and the system was capable of reaching 1200°C in less than 3min with the help of SiC. The results of synthesis technique prior to the microwave heating indicated that the samples start to crystallize after 5min. The X-ray diffraction (XRD) data indicated that the sample was polycrystalline and acquires the host structure. The Photoluminescence (PL) and Photoluminescence Excitation (PLE) spectra for the powder phosphor prepared showed similar results as those prepared using the conventional method. The Y_2O_3 powder samples doped with Eu showed strong red emission at 630nm, the Tb doped samples showed a strong green emission at 550nm and Tm doped samples showed blue emission at 460nm. According to analysis by using Scanning Electron Microscope (SEM), the crystal size of the microwave irradiated samples was smaller in comparison to those prepared using the conventional method (this may be due to shorter heating time). The results indicated that the microwave heating technique was a reliable, fast and suitable technique to produce these phosphors. The characteristics of the phosphor were as good as those prepared using the conventional heating technique. [9]

Kulkarni et al., in 2006, focused studies on REEs in atmospheric fine particles and their sources. $\text{PM}_{2.5}$ samples were collected from an ambient air quality-monitoring site located in the proximity of a large number of oil refineries and petrochemical industries to estimate the potential contributions of emissions from fluidized-bed catalytic cracking operations to ambient fine particulate matter. Several commercially available zeolite catalysts were used and local soil was measured after microwave assisted acid digestion using inductively coupled plasma—mass spectrometry. Source identification and apportionment was performed by principal component factor analysis (PCFA) in combination with multiple linear regression. The REEs relative abundance sequence, ratios of La to light REEs (Ce, Pr, Nd and Sm), and enrichment factor analysis indicated that refining and petrochemical cat cracking operations were predominantly responsible for REEs enrichment in ambient fine particles. The PCFA yielded five physically meaningful $\text{PM}_{2.5}$ sources: cat cracking operations, a source predominantly comprised of crustal material, industrial high temperature operations, oil combustion and sea spray. These sources accounted for 82% of the total mass of atmospheric fine particles (less carbon and sulfate). Factor analysis confirmed that emissions from cat cracking operations primarily contributed to REEs enrichment in $\text{PM}_{2.5}$ even though they comprised only 2.0% of the apportioned mass.

Results from this study demonstrated the need to characterize catalysts employed in the vicinity of the sampling stations to accurately determine local sources of atmospheric REEs. [10]

Kulkarni et al., in 2007, developed a microwave-assisted acid digestion procedure followed by inductively coupled plasma-mass spectrometry (ICP-MS) to quantify rare earth elements (REEs) in fluidized-bed catalytic cracking (FCC) catalysts and atmospheric fine particulate matter (PM_{2.5}). High temperature (200°C), high pressure (200psi), acid digestion (HNO₃, HF and H₃BO₃) with 20min dwell time effectively solubilized REEs from six fresh catalysts, a spent catalyst and PM_{2.5}. This method was also employed to measure 27 non-REEs including Na, Mg, Al, Si, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Mo, Cd, Cs, Ba, Pb and U. Complete extraction of several REEs (Y, La, Ce, Pr, Nd, Tb, Dy and Er) required HF indicating that they were closely associated with the aluminosilicate structure of the zeolite FCC catalysts. Internal standardization using ¹¹⁵In quantitatively corrected non-spectral interferences in the catalyst digestate matrix. Inter-laboratory comparison using ICP-optical emission spectroscopy (ICP-OES) and instrumental neutron activation analysis (INAA) demonstrated the applicability of the newly developed analytical method for accurate analysis of REEs in FCC catalysts. The method developed for FCC catalysts was also successfully implemented to measure trace to ultra-trace concentrations of La, Ce, Pr, Nd, Sm, Gd, Eu and Dy in ambient PM_{2.5} in an industrial area of Houston, Texas. [11]

Ma et al., in 2007, reported a facile method to prepare hollow PrF₃ nanoparticles by microwave-assisted heating hydrothermal process. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). It was found that the PrF₃ nanoparticles had closed-cage hollow sphere-like morphology, high crystallinity and purity with the mean size of about 31nm. The microwave-assisted hydrothermal process may be a better synthesis option for preparing rare earth fluorides nanoparticles than the conventional hydrothermal method. Water is an excellent microwave-absorbing agent and can be rapidly heated under microwave irradiation due to its high dielectric constant and microwave susceptibility. Therefore, the suspension of freshly-prepared PrF₃ colloidal precipitates can be rapidly heated by this way, which results in the gradual dissolving of the PrF₃ colloidal precipitate precursor. [12]

3. CONCLUSIONS

Several rare earth elements (REEs) can be associated with microwave technology to increase the speed of the reactions in different chemical compounds, generally actuating as catalysts, and consequently reducing the reaction times.

This technology has been successfully used in these materials, but there are some discussions whether the reaction rates are enhanced due to faster and selective dielectric heating provided by this technique or due to any specific effect (e.g.: specific bond activation). Compared to other heating methods, substances with high dielectric loss factor (ability of the substance to absorb the electromagnetic energy), such as REEs, can couple easily with microwave radiation and gets heated.

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