Materials Science Forum Vol. 754 (2013) pp 89-97

doi:10.4028/www.scientific.net/MSF.754.89

A Novel Sonochemical Synthesis of Metal Oxides Based Bhasmas

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Keywords. Ayurveda, bhasma, tamra bhasma, metal oxides, ultrasound, sonochemical, unit operations , unit processes, green chemistry.

Abstract. Metal oxides form part of inorganic medicines called Bhasmas, which has been used in a non-allopathic medicine system practiced in India called Ayurveda. Bhasmas may be classified under the nano medicines of ancient India. The traditional preparation methods involve time consuming and complicated preparation procedures. This paper highlights a novel ultrasound assisted technique called sonochemical synthesis of transition metal oxides in a facile, faster, inherently safer and environmentally benign (green chemistry) way which could be considered to be used for the synthesis of metal oxides such as copper oxide which form part of the copper based Ayurvedic nano medicine called tamra bhasma, which is copper in its oxide form and used therapeutically as a source of copper. The synthesis procedure outlined here could be considered for the preparation of other types of Bhasmas also.

Introduction

A chemical reaction involves the transformation of molecular bonds and the temperature and pressure required for driving chemical reactions may be supplied either directly through conventional energy sources as thermal, pressure energies or indirectly through alternate energy sources such as microwave and ultrasound energies. The ultrasound (sonochemical) technique utilizes the principle of acoustic cavitation, which involves the formation, growth and violent implosions of micro cavities inside liquids irradiated with ultrasound. These regions where implosions occur are called hotspots. The result of cavitation (due to implosion of cavities) is the facile creation of supercritical conditions of very high pressures and temperatures of about 1000 atm and 5000 K respectively along with very fast heating and cooling rates of the order of 10^{12} K/sec and besides intense turbulence conditions are generated in the liquid. The supercritical conditions created by ultrasound energy is on the time-scale of nano seconds and is restricted to micro scale size regions called hot spots, ensuring inherent safety to the sonochemical processes [1-14]. Therefore the sonochemical route could emerge in a big way as an alternate route for conducting the unit operations (physical processes) and unit processes (chemical reactions) of chemical engineering in a safer and environmentally benign way [15-16].

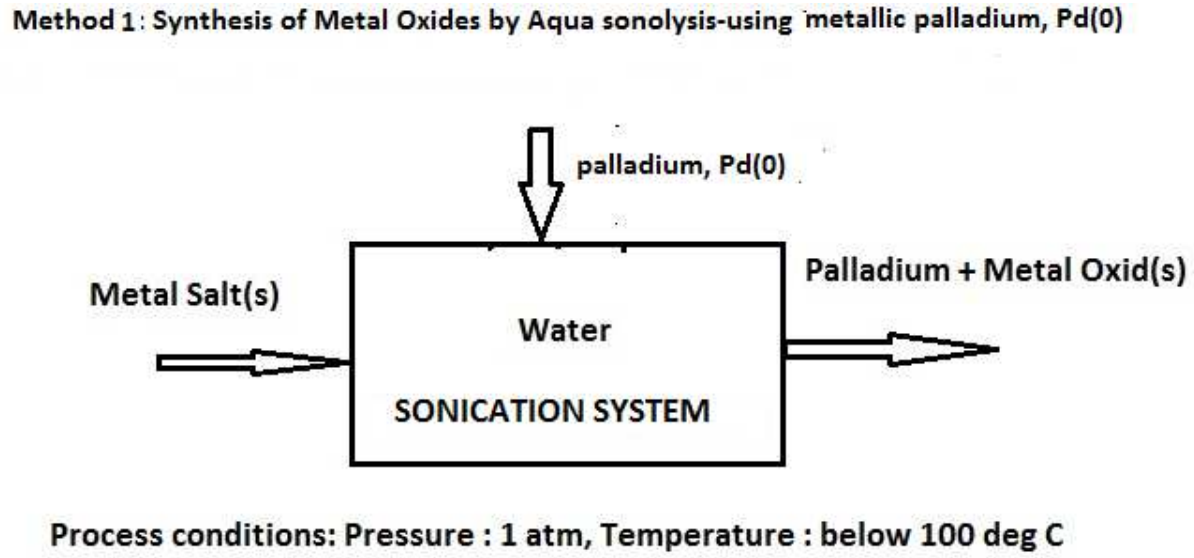
The physical and chemical effects produced by ultrasound in liquids could be explored to enhance the efficiency of unit operations and unit processes which are involved in the synthesis of chemicals including medicinal compounds. Ultrasound energy could be easily applied to the various stages in the preparation of herbal medicines, such the mixing and extraction of chemicals from plants etc. Ultrasound could also be very beneficial for driving many chemical reactions involved in the preparation of both the organic herbal medicines and inorganic medicines such as Bhasmas in a facile, faster, environmentally benign and energy efficient way.

Bhasmas, which are commonly used in Ayurvedic System of medicine, may be classified under inorganic medicines. In general metal oxides based Bhasmas have been used for treating various diseases and also as preventive medicines. Bhasmas may be considered as the ancient nanomedicines

of Ayurveda. Bhasmas preparation is a time-consuming and complicated process involving the purification and grinding together of a number of herbs, juices, along with metal/ metal compounds required for the making of Bhasmas. Finally the slurry obtained is calcined in a complicated procedure to get the dry powder of Bhasmas [17-20]. The novel, facile and environmentally benign sonochemical technique outlined here could shorten the processing time, reduce the number of chemicals used and energy requirement leading to reduction in the cost of making the traditional Bhasmas containing the metal oxides. Consequently the use of sonochemical technique could offer a novel and an efficient alternate way to prepare the herbal medicines and Bhasmas. A novel procedure for the synthesis of palladium based metal oxides by sonication is presnted [21].

Experimental

The synthesis procedure is very simple and requires just the green solvent water and palladium as the chemicals. When palladium salts are used as precursors, ethanol is required as the reducing agent. These two types of synthetic processes are outlined in the following figures. The synthesis could be carried out in any kind of sonication equipments such as the probe-type direct sonicator or the bath-type indirect sonicator.



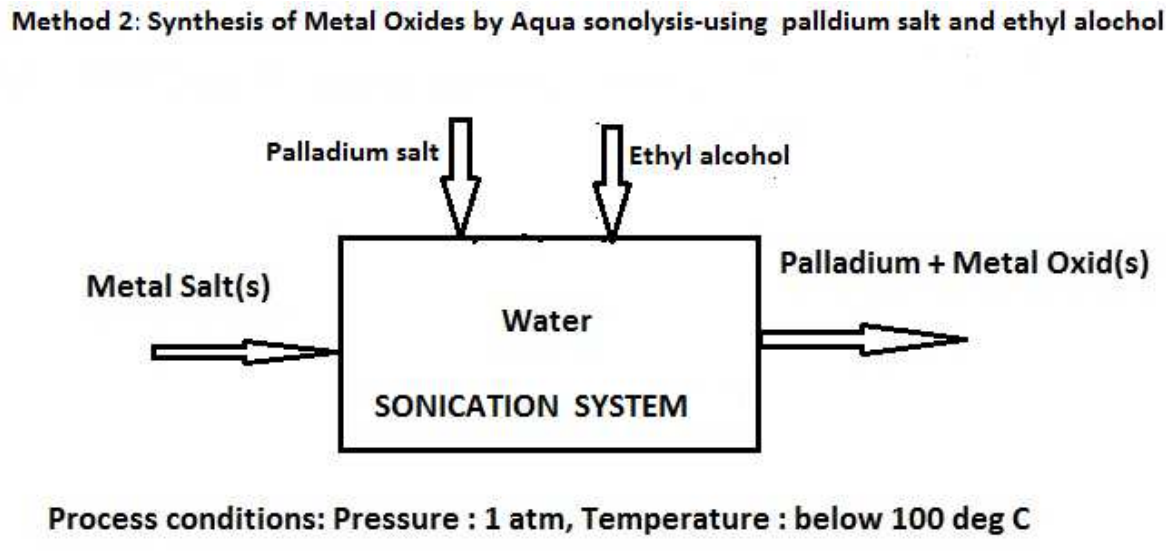


Fig.1. The two types of synthetic schemes useful in the preparation of metal oxides [21].

Materials: Chemicals & Equipments
A typical synthesis procedure is given below for the preparation of copper oxide [21].

Inorganic (metal) salt precursors. The type of inorganic precursors used in the synthesis depends on the metallic oxides to be synthesized, which includes precursors with organic / inorganic ligands such as nitrates, sulphates, acetates etc. Typically for synthesizing copper oxide- copper acetate, copper nitrate and copper sulphate were successfully tried.
Other chemicals required. Palladium was used either as pure metallic palladium Pd (0) or as palladium salts such as palladium acetate and palladium nitrate. Ethanol was used as the reducing agent to synthesise palladium when palladium salts were used. The sonication medium used was the green solvent water.
Sonication equipments. A SONICS make 750W ultrasonic processor with 13.2 mm diameter probe operating at 20 kHz frequency was used for direct sonication. A MARK make ultrasonic bath (32 kHz) was utilized for indirect sonication. A 100 ml glass vessel was used as the batch sonochemical reactor and the air supply to this reactor was provided by an aquarium pump.
Method of Synthesis of metal oxides.

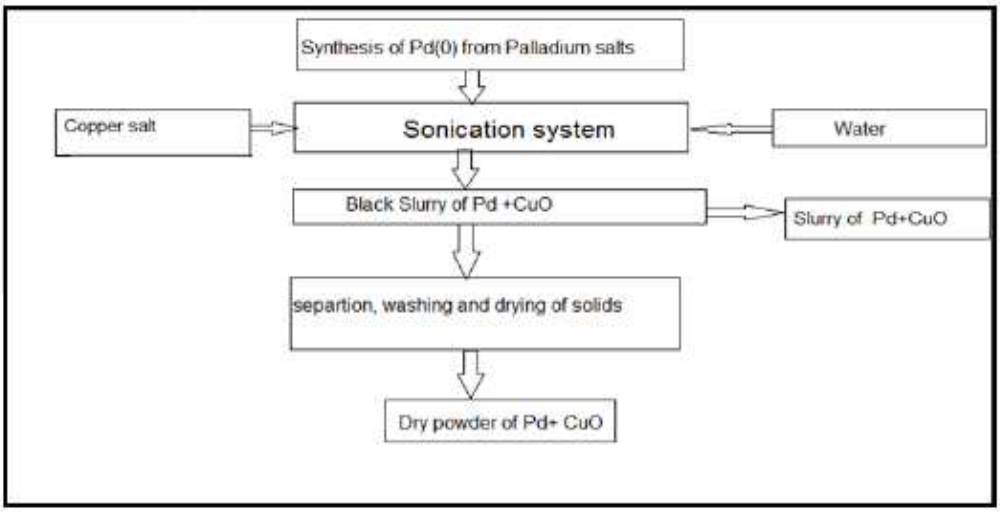


Fig. 2. Flow diagram of the synthsis process of Pd+CuO.

Preparation of Pd (0)-water slurry. Palladium [Pd (0)] was dispersed in 90 ml water to make Pd-water slurry by sonicating for about 5 mins. This simple system of Pd-water slurry irradiated with ultrasound was used for the synthesis of the transition metal oxides from their precursors such as transition metal salts. When palladium salts were used, a mixture of 20 mL ethanol and 70 mL water was used for making Pd-water slurry.

Synthesis of Pd(0)-metal oxide slurry. Typically for the synthesis of CuO, copper acetate was used as the metal salt precursor. Copper acetate was added to the Pd(0)-slurry and sonication continued for the given time by the combination of indirect-sonication in a sonicator bath (32 kHz) and for direct-sonication in a sonotrode (20 kHz). Air supply was provided to the reaction mixture by using an aquarium pump. Experimental parameters such as temperature (non-isothermal operation) and pH of the slurry were measured (Table 1). The experimental parameters (process conditions) used were given in Table-1. Four parameters such as the mass ratio of palladium metal to metal salt, %amplitude, switch on & switch off time in the pulse mode of sonication, duration of sonication were varied in 4 levels.

Table 1. Process conditions used for the sonochemical synthesis of copper (II) oxide.

Run No.	Pd(0) : Cu(Ac)2 (g) : (g)	% Amplitude	ON (sec)/ OFF(sec)	Sonicati-on Time (min)	Initial pH	Final pH	Initial temp. (°C)	Final temp. (°C)	Average particle size (microns)
1	0.08 : 0.40	30	5 / 1	10	5.67	5.62	27	38	1.29
2	0.08 : 0.40	35	5 / 2	20	5.59	5.42	29	47	0.80
3	0.08 : 0.40	40	5 / 3	30	5.64	5.42	30	57	2.82
4	0.08 : 0.40	45	5 / 4	40	5.43	5.23	29	62	3.31
5	0.09 : 0.45	30	5 / 2	30	5.03	4.91	30	52	3.59
6	0.09 : 0.45	35	5 / 1	40	5.49	5.38	31	58	3.70
7	0.09 : 0.45	40	5 / 4	10	5.39	5.31	33	47	5.70
8	0.09 : 0.45	45	5 / 3	20	5.56	5.36	29	53	3.15
9	0.10 : 0.50	30	5 / 3	40	5.38	5.25	29	55	4.80
10	0.10 : 0.50	35	5 / 4	30	5.57	5.43	30	55	3.69
11	0.10 : 0.50	40	5 / 1	20	4.67	4.59	31	47	4.73
12	0.10 : 0.50	45	5 / 2	10	4.75	4.67	31	49	3.83
13	0.11 : 0.55	30	5 / 4	20	5.03	4.98	31	49	4.28
14	0.11 : 0.55	35	5 / 3	10	4.49	4.44	31	44	3.10
15	0.11 : 0.55	40	5 / 2	40	5.44	4.89	31	63	4.25
16	0.11 : 0.55	45	5 / 1	30	5.28	4.85	32	62	1.99

The chemical reactions involved in the synthesis. Palladium salt was reduced to palladium by ethyl alcohol [eq.1]. Alternately palladium metal was used directly. Palladium catalysed the formation of "sono" H_2O_2 from the "sono" hydrogen produced during the sonolysis of water [22]. These "sono" H_2O_2 converts the metal salts into their corresponding metal oxides [eq.2]. Thus palladium, water and ultrasound energy were used to convert transition metal salts into their oxides [eq. 3].

$$\text{Pd (2+)} + \text{Alcohol} + \text{Water} \longrightarrow \text{Pd (0)} \qquad (1)$$

$$H_2O \xrightarrow{)))} H^{\cdot} + {}^{\cdot}OH$$

$$^{\cdot}H + {}^{\cdot}H \longrightarrow H_2$$

$$^{\cdot}OH + {}^{\cdot}OH \longrightarrow H_2O_2$$

$$\text{Metal Salt(s)} \xrightarrow{H_2O_2} \text{Metal Oxides} \qquad (2)$$

Overall reaction:

$$\text{Metal Salt(s)} \xrightarrow[\text{Pd (0)}\quad H_2O]{))))} \text{Metal Oxide(s)} \qquad (3)$$

Synthesis of dry bulk metal oxides. The Pd-based metal oxides produced can be used as aqueous slurries or it can alos be dried to get the powder. A Pd-based metal oxide slurry may be centrifuged and/or heated to remove volatiles and produce the dry Pd-based metal oxide powder. Thus a green synthesis procedure using ultrasound energy has been developed for synthesising a series of palladium based mono and multi metal oxides such as Pd-Cu-O, Pd-Fe-O, Pd-Co-O, Pd-Mn-O, Pd-Ni-O, Pd-Cu-Mn-O, Pd-Cu-Ni-O etc. The presence of sulphur and carbon in the metal oxides was avoided by using non-sulphur, non-carbon containing metal precursors. The synthesis of Pd- based metal oxides by this sonochemical process is a novel, facile, green, faster and inherently safer process as compared to the existing processes for the synthesis of metal oxides [21].

Characterisation of bulk metal oxides. Dry Pd-based metal oxides were characterized using SEM-EDX, XRD and DLS methods to determine the chemical composition, crystal structure, average particle size and distribution.The results of characterisation of a typical sample of Pd-CuO powder (Table 1, Run no.2) are given in Figs 3-6.

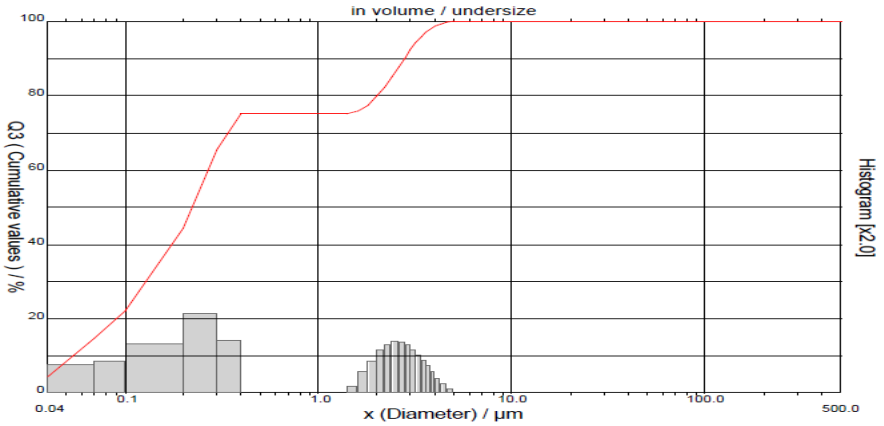


Fig. 3. Particle size distribution using DLS technique by CILAS 1064 particle size analyser -shows formation of both nano and micro particles.

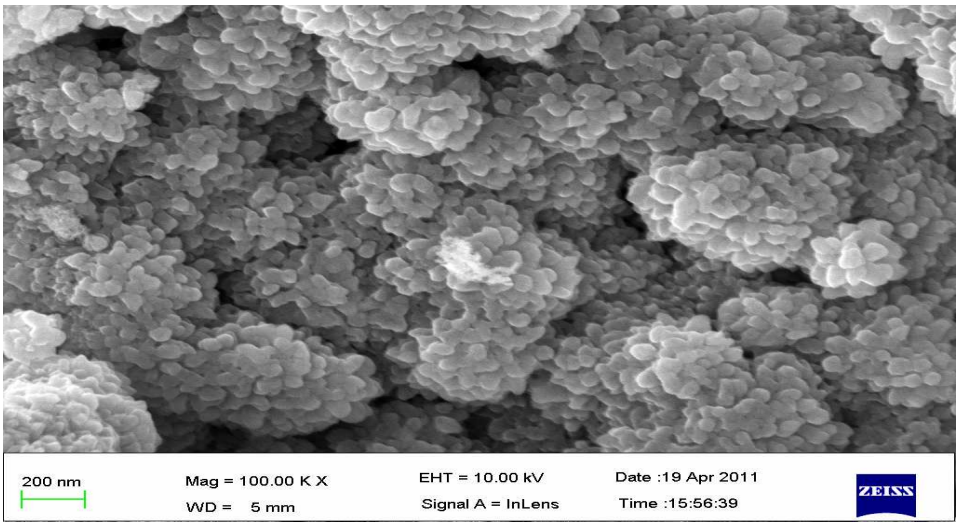
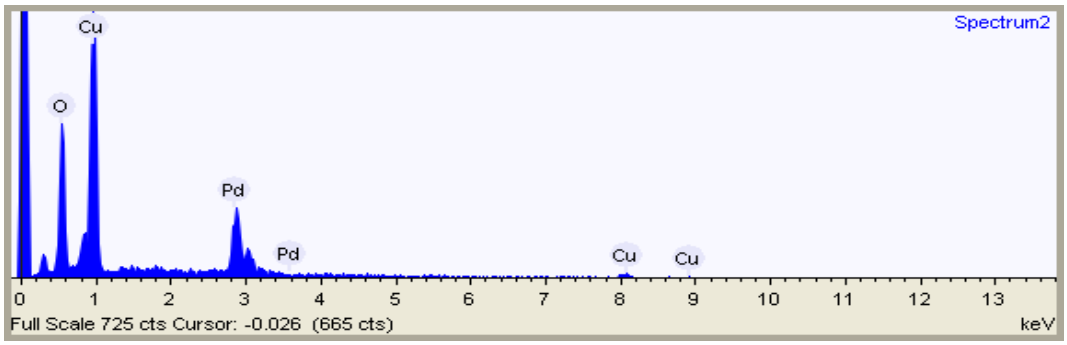


Fig.4 SEM micrograph- shows flower like repeating pattern of particles.



Element	Weight %	Weight % σ	Atomic %
Oxygen	20.751	0.756	54.663
Copper	52.202	1.067	34.624
Palladium	27.047	1.128	10.713

Fig. 5. EDX analysis – confirms the presence of Pd, Cu and O atoms.

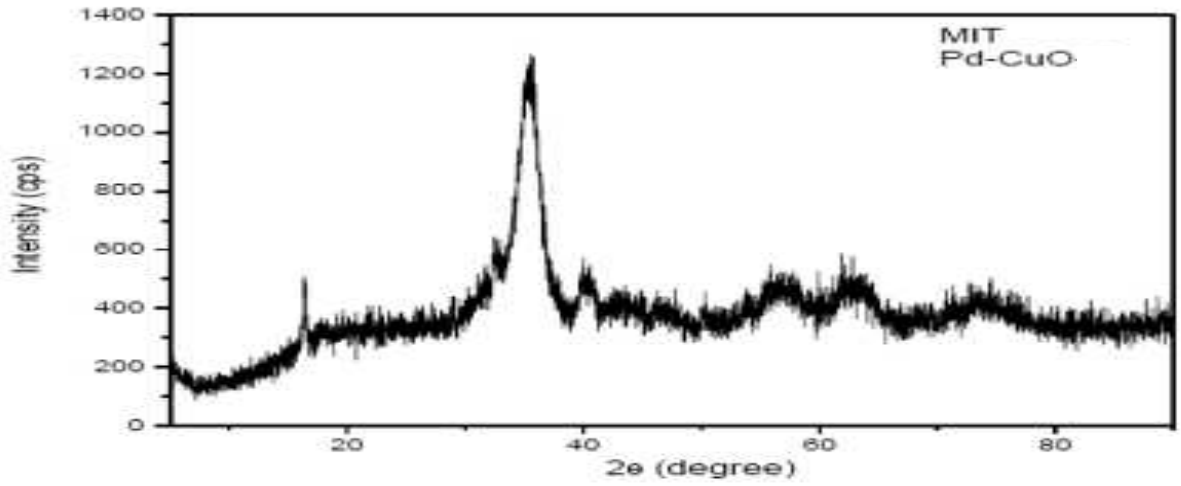


Fig. 6. XRD spectra- confirm the phases as palladium and copper (II) oxide.

The peaks at 40.22, 46.68, 68.44, 82.6 and 86.7 were indexed to the (111), (200), (220), (311) and (222) planes of Pd in FCC lattice (JCPDS file no. 89-4897). The peaks centered at 2θ values of 32.45, 35.42, 35.42, 38.29, 38.99, 57.16 and 62.98 could be indexed to the (110), (111) (002), (111), (200), (202) and (113) planes of CuO in monoclinic system (JCPDS file no. 89-2531).

Conclusion

The characterisation of the samples by DLS revealed the formation of both nano and microparticles with average size ranging from 0.8 micron to 5.7 micron. The typical SEM micrograph for 0.8 micron size particles showed flower like repeating pattern. The EDX spectra showed the elemental composition of surface was made up of atoms of palladium, copper and oxygen. The XRD spectra confirmed the phases as palladium and copper (II) oxide. This novel sonochemical synthesis of metal oxides could be explored as an alternate way to make metal oxide based Bhasmas. Though the palladium based metal oxides may be used directly as dental materials, experiments are underway to minimize / totally eliminate the amount of palladium present with the metal oxides synthesized to be used as Bhasmas. Pure metal oxides free of palladium may be synthesised by using novel reactor designs. Further standard clinical trials are required to confirm the safety, efficacy and quality of the herbal medicines and metal oxides based Bhasmas prepared by the non-conventional method using the alternate ultrasound energy. Since the particle size plays a key role in any heterogeneous chemical reactions, the efficacy and safety of this sonochemically synthesised Bhasma with respect to particle size also have to be systematically investigated in detail.

In India metallic materials such as copper, tin, silver, gold etc. have been used as utensils for external use along with the metallic Bhasmas as internal medicines from ancient times. Now there is an urgent need for the practitioners of the modern and traditional systems of medicine to work together to standardise the synthesis procedures for the quality, safety and efficacy of these metal based medicines [23]. The humanity will benefit enormously if we could build a “Golden Triangle” between Modern Science & Technology, Modern Medicine and Ancient Medicine such as Ayurveda [24].

References

[1] Publication list of Suslick http://www.scs.illinois.edu/suslick/publications.html.

[2] Hielscher-UltrasoundTechnology,http://www.hielscher.com/ultrasonics/sonochem_01.htm.

[3] Sonochemistry Centre, Coventry University, UK, http://www.sonochemistry.info/index.htm.

[4] L.H. Thompson, L.K. Doraiswamy, Sonochemistry: Science and Engineering, Ind. Eng.Chem. Res. 38 (1999) 1215-1249.

[5] T.J. Mason, Ultrasound in synthetic organic chemistry, Chem. Soc. Rev. 26 (1997) 443-451.

[6] Y.T. Shah, A.B. Pandit, V.S. Moholkar, Cavitation Reaction Engineering, Kluwer Academic/ Plenum Publishers, New York (1999).

[7] P. Cintas, J.L.Luche, Green chemistry-The sono chemical approach, Green Chemistry,June 1999,115-125.

[8] G. Cravotto, P. Cintas, Power ultrasound in organic synthesis: moving cavitational chemistry from academia to innovative and large-scale applications, Chem. Soc. Rev. 35 (2006) 180-196.

[9] K.S. Suslick, The Chemistry of Ultrasound, The Yearbook of Science & the Future Encyclopaedia Britannica: Chicago, 1994; pp 138-155.

[10] S.K. Suslick, G. Price, Applications of Ultrasound to Materials Chemistry, Annu. Rev. Matl. Sci. 29 (1999) 295-326.

[11] K.S. Suslick, D.A. Hammerton, R.E.Jr. Cline, The Sonochemical Hot Spot, J. Am. Chem. Soc. 108 (1986) 5641-5642.

[12] E.B. Flint, K.S. Suslick, The Temperature of Cavitation,Science, 253 (1991)1397-1399.

[13] K.S. Suslick, The Chemical Effects of Ultrasound, Scientific American, February 1989 pp.62-68.

[14] Y. Son, M. Lim, M. Ashokkumar, J. Khim, Geometric Optimization of Sonoreactors for the Enhancement of Sonochemical Activit, J. Phys. Chem. C 115 (2011) 4096-4103.

[15] Green chemistry, a US EPA program, http://www.epa.gov/greenchemistry/pubs/educat.html.

[16] G. Centi, S. Perathoner, Catalysis and sustainable (green) chemistry, Catal. Today 77 (2003) 287-297.

[17] P.K. Sarkar, A.K. Chaudhary, Ayurvedic Bhasma: the most ancient application of nanomedicine, J. Sci. Ind. Res., 69(12) (2010) 901-905.

[18] K. Chitnis, A. Stanley, Chemical Evaluation of Tamra Bhasma, Int. J. Pharma. Bio. Sci. 2(2) (2011) 160-168.

[19] MP. Wadekar, C.V. Rode, Y.N. Bendale, K.R. Patil, A.A. Prabhune, Preparation and characterization of a copper based Indian traditional drug: tamra bhasma, J. Pharm. Biomed. Anal. 39(5) (2005) 951-955.

[20] M.P. Wadekar, C.V. Rode, Y.N. Bendale, K.R. Patil, A.B. Gaikwad, A.A. Prabhune, Effect of calcination cycles on the preparation of tin oxide based traditional drug: Studies on its formation and characterization, J. Pharm. Biomed. Anal. 41(4) (2006) 1473-1478.

[21] S. Sivasankaran, Synthesis of Palladium Based Metal Oxides by Sonication, Patent application numbers: INDIAN: 2042 / CHE / 2011, PCT: IB 2011 / 053412, US: 13 / 498,556.

[22] G. Centi, F. Cavani, F. Trifirò, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic/ Plenum Publishers, New York, 2001.

[23] N.J. Gogtay, H.A. Bhatt, S.S. Dalvi, N.A. Kshirsagar, The Use and Safety of Non-Allopathic Indian Medicines, Drug Safety 25(14) (2002) 1005-1019.

[24] R.A. Mashelkar, Ayurveda for the Future-Inaugural Address: Part I, Second World Ayurveda Congress, Advance Access Publication, 5(2) (2208) 129-131. 10.1093/ecam/nen013