JOURNAL OF MATERIALS SCIENCE **39** (2004) 723–726

Microwave synthesis of metal phthalocyanines under solvent-free conditions

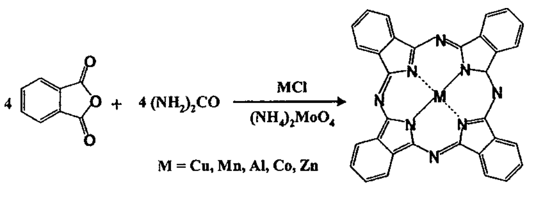
KI SUCK JUNG, JONG HO KWON
Phthalos Co., Pukyong Technocomplex, Pukyong National University, Busan 608-739, Korea

SE MO SHON
Division of Image & Information Engineering, Pukyong National University, Busan 608-739, Korea

JIN PHIL KO, JUN SIK SHIN, SEONG SOO PARK
Division of Chemical Engineering, Pukyong National University, Busan 608-739, Korea
E-mail: sspark@pknu.ac.kr

An efficient microwave processing has been developed for the synthesis of metal phthalocyanines (MPc: $M = $ Cu, Mn, Al, Co and Zn) through the condensation reaction of phthalic anhydride and urea with various metal chlorides in the presence of ammonium molybdate catalyst under solvent-free condition using microwaves, as a green chemistry procedure.

Phthalocyanines have been intensively investigated since the first synthesis in 1907, and extensively used as blue and green dyestuffs due to their unique properties of being very stable against thermal or chemical decomposition and very intense optical absorption in the visible region [1, 2]. Recently, their use as a photoconducting material in photocopying machines has provoked research in various fields of sensor, electro-chromic display devices, photovoltaic cells, xerography, semiconductor, catalysis, nonlinear optics, etc. [3–5]. Specificity in their applications can be introduced by the modification of large and flat π-conjugation system of phthalocyanines and the change of central metals [6, 7]. Phthalocyanines can be obtained by the classical template reactions starting from diverse precursors, such as phthalonitrile, dicyanobenzene, cyanobenzamide, phthalimide and phthalic acid, with metal salts in high-boiling nonaqueous solvent at elevated temperature as shown in an Equation 1 [8, 9].



(1)

Microwave processing has attracted potential as an alternative to classical thermal processing because of the inherent advantage of microwave heating, which is selective, direct, rapid, internal, and controllable [10–12]. In many organic syntheses, the microwave processing has been used in combination with solvent-free condition to improve organic synthesis, leading to shorter reaction time, higher yield, and easier work-up than the classical thermal processing [13–16]. The acceleration of reactions by microwaves can result from material-microwave interaction leading to thermal and non-thermal effect; the thermal effect caused by microwaves is mainly due to dipolar and ionic polarization, although conduction losses can also be important at high temperature. The non-thermal effect associated with microwaves may be due to the increase of probability of molecular impact, the decrease of activation energy, and the intervention of localized microscopic high temperature. Despite the abundance of reported data on synthesis of phthalocyanines, there is no information in the available literature on the use of microwave processing to obtain phthalocyanines in the condition of use of urea and phthalic anhydride as the cheapest phthalocyanine precursors. In this paper, we described a facile three-component and one-pot condensation reaction of various metal phthalocyanines using microwaves under solvent-free condition, which was adaptable for the synthesis of new phthalocyanine derivatives.

Phthalic anhydride (Junsei Chemical Co.), urea (Katayama Chemical Co.), metal chloride (Katayama Chemical Co.), and ammonium molybdate (Junsei Chemical Co.) were used as supplied. The general procedure employed for syntheses of various metal phthalocyanines was described as; 42 g of phthalic anhydride, 49 g of urea, and 7 g of metal chloride with 0.1 g of ammonium molybdate as a catalyst were charged together into a 3-neck reaction flask. The reaction flask was placed in a microwave synthetic unit fitted with a modified thermocouple, a reflux condenser, and a motor-driven stirrer. Reactant was uniformly mixed and gradually heated up to 120 °C with heating rate of 5 °C/min, and then heated to between 170 and 230 °C with heating rate of 2 °C/min. It was maintained at those temperature ranges for 0.5 to 4 h with the stirring speed of about 100 rpm. Reaction product was washed with methyl alcohol. After filtration, it was acid-treated for 1 h by 100 ml of 0.02 M H_2SO_4 solution, alkali-treated for 1 h by 100 ml of 0.02 M NaOH solution, then washed with hot distilled water until washing solution became neutral. After filtration, it was dried at 105 °C over 24 h in a dry oven, whereupon final product was obtained.

To find effective reaction condition for the synthesis of metal phthalocyanines, the effect of reaction

0022–2461

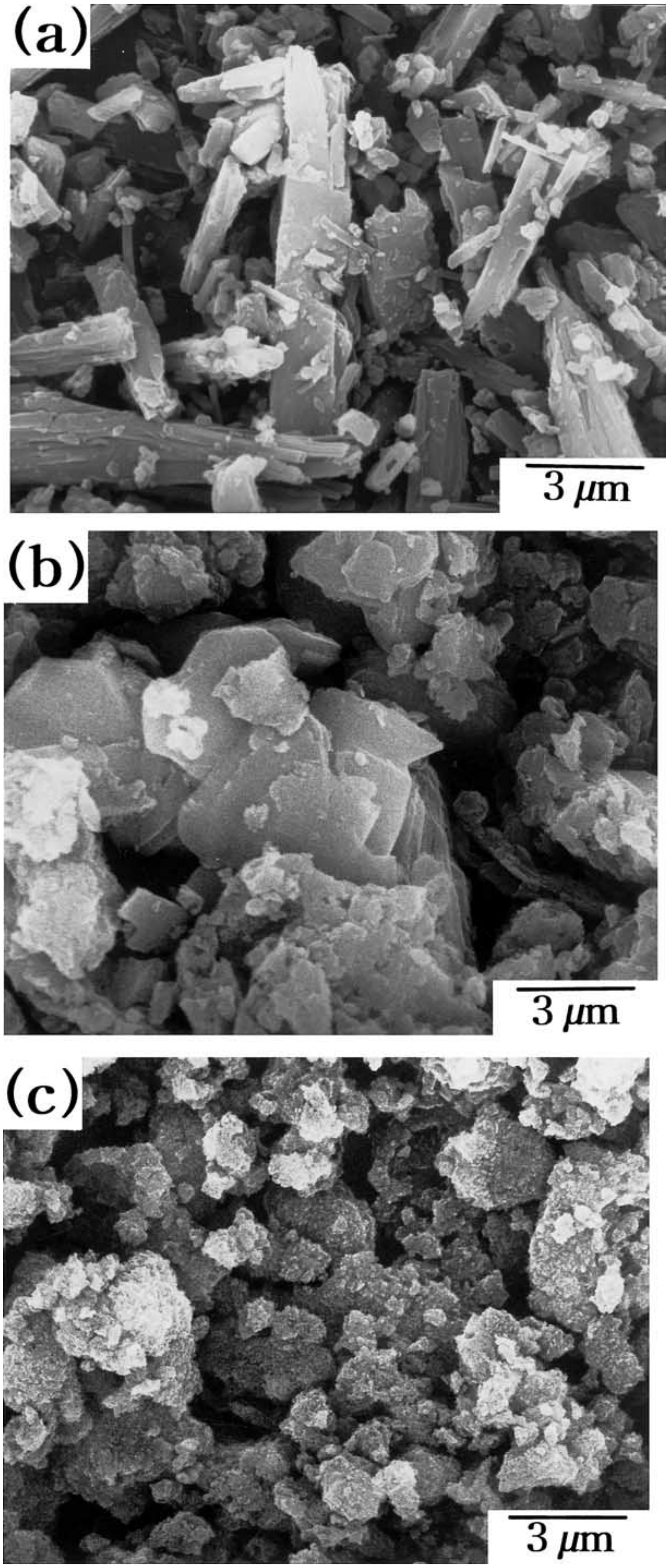


Figure 1 SEM pictures of metal phthalocyanines (MPc: $M = \mathrm{Cu}$, Mn, Al, Co and Zn) synthesized at 230 °C for 2 h using microwave irradiation under solvent-free condition ((a) CuPc, (b) MnPc, (c) AlPc, (d) CoPc, and (e) ZnPc). (*Continued*)

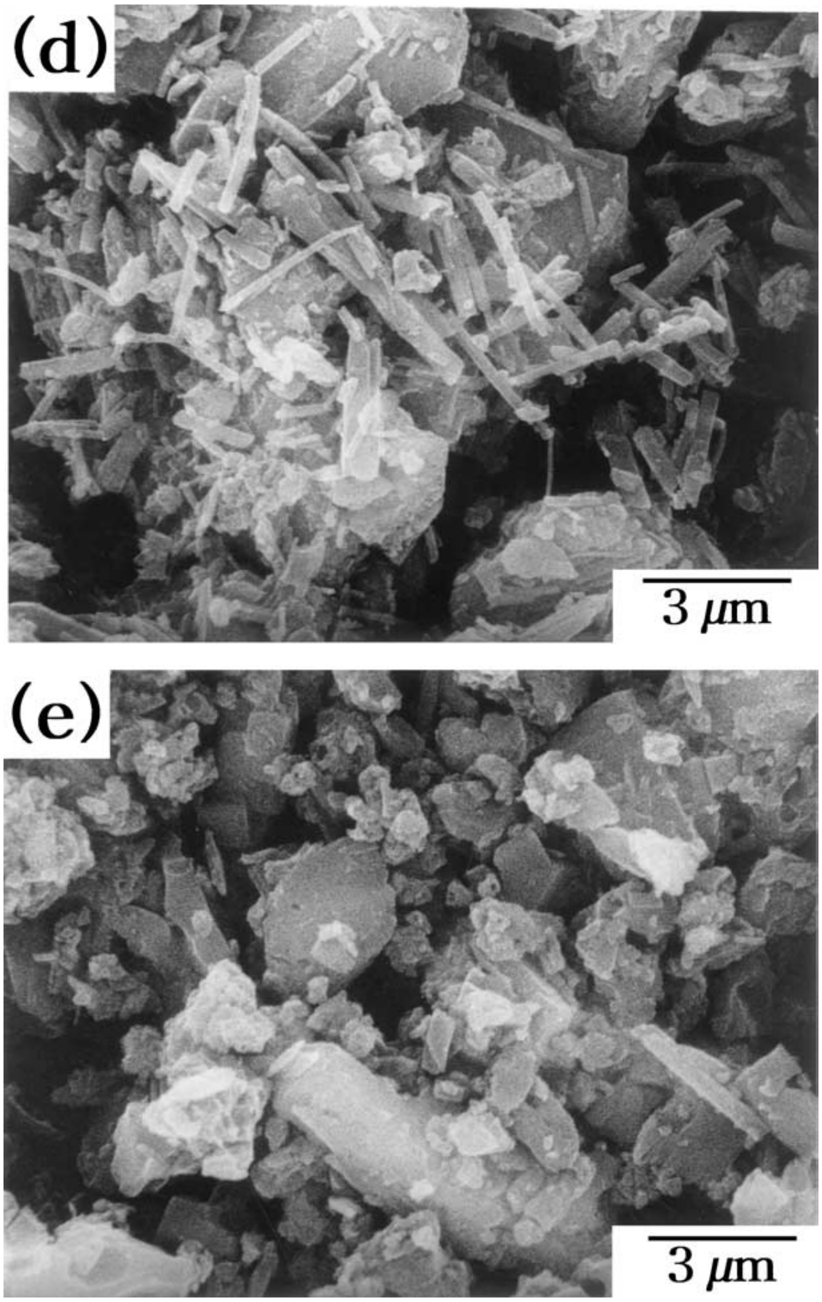


Figure 1 (*Continued*).

temperature and time on the synthesis of copper phthalocyanines was examined at solvent-free condition under microwave irradiations. The data presented in Table I clearly showed that phthalic anhydride and urea reacted effectively with copper chloride in the presence of ammonium molybdate at various temperatures for various times without using the solvent as medium of heat transfer. Therefore, the yield of copper phthalocyanines, ranging from 73 to 81%, increased below 210 °C and did not further increase above 210 °C for given time of 2 h with increasing reaction temperature. Also, the yield of copper phthalocyanines increased with increasing reaction time at the fixed temperature of 230 °C.

TABLE I Yield and purity of copper phthalocyanines synthesized at various conditions using microwave irradiation under solvent-free conditions

Reaction temperature (°C)	Reaction time (h)	Yield (%)	Purity (%)
170	2.0	73	94
190	2.0	77	94
210	2.0	82	95
230	0.5	76	94
230	1.0	77	94
230	2.0	81	95
230	4.0	81	95

From above results, the syntheses of metal phthalocyanines (MPc: $M = \mathrm{Cu}$, Mn, Al, Co and Zn) were conducted at 230 °C for 2 h with solvent-free condition under microwave irradiations. The data presented in Table II clearly showed that metal phthalocyanines were synthesized successfully in good yield, ranging from 62 to 81%. The yields of metal phthalocyanines were different according to the kind of metal. SEM pictures shown in Fig. 1 illustrated that morphologies of metal phthalocyanines were quite different from the

TABLE II Yield of metal phthalocyanines (MPc: M = Cu, Mn, Al, Co and Zn) synthesized at optimum conditions using microwave irradiation under solvent-free conditions

Metal	Reaction temperature (°C)	Reaction time (h)	Yield (%)
Cu	230	2	81
Mn	230	2	78
Al	230	2	69
Co	230	2	64
Zn	230	2	62

kind of metal. It was due to different reactivity of metal chloride during reaction. As above results, it was assumed that microwave process under solvent-free condition can be expected to produce more-efficient and clean synthesis of metal phthalocyanines by lowering the activation energy required the reaction between the reactive species shown in Equation 1 due to intense internal heating, together with differential polarization effect [14].

In conclusion, the present three-component one-step procedure described in this paper demonstrated that microwave processing combined with solvent-free condition leads to shorter reaction time, higher yield, clean reaction product and easier work-up than classical thermal processing. It was thought that our work is a further example of the commercial application of microwaves for organic synthesis.

Acknowledgments

This work was supported by grant of Human Resource Development in Industrial Technology from Korea Industrial Technology Foundation.

References

1. N. B. McKEOWN, in “Phthalocyanine Materials” (University Press, Cambridge, 1998) p. 12.
2. A. L. THOMAS, in “Phthalocyanines, Research and Application” (CRC Press, Boca Raton, 1990) p. 37.
3. J. JIANG, D. P. ARNOLD and H. YU, *Polyheron* **18** (1999) 2129.
4. A. S. DRAGER and D. F. O’BRIEN, *J. Org. Chem.* **65** (2000) 2257.
5. G. A. KUMAR, G. JOSE, V. THOMA, N. V. UNNIKRISHNAN and V. P. N. NAMPOORI, *Spectrochimica Acta* A **59** (2003) 1.
6. B. HASSAN, H. LI and N. B. McKEOWN, *J. Mater. Chem.* **10** (2000) 39.
7. P. MATLABA and T. NYOKONG, *Polyhedron* **21** (2002) 2463.
8. B. I. KHARISOV, L. M. BLANCO, L. M. TORRES and A. GARCIA, *Ind. Eng. Chem. Res.* **38** (1999) 2880.
9. W. HERBST and K. HUNGER, “Industrial Organic Pigments” (VCH, New York, 1993) p. 417.
10. H. M. KINGSTON and S. J. HASWELL, in “Microwave-Enhanced Chemistry” (Amer. Chem. Soc., Washington DC, 1997) p. 3.
11. W. H. SUTTON, *Amer. Ceram. Soc. Bull.* **68** (1989) 376.
12. S. S. PARK, E. H. HWANG, B. C. KIM and H. C. PARK, *J. Amer. Ceram. Soc.* **83** (2000) 1341.
13. A. LOUPY, P. PIGEON and M. RAMDANI, *Tetrahedron* **52** (1996) 6705.
14. A. QUSSAID, E. PENTEX and A. LOUPY, *New J. Chem.* **231** (1997) 1339.
15. A. VASS, J. DUDAS, J. TOTH and S. VARMA, *Tetrahedron Lett.* **42** (2001) 5347.
16. B. KABOUDIN and R. NAZARI, *ibid.* **42** (2001) 8211.
17. S. CADDICK, *Tetrahedron* **51** (1995) 10432.
18. D. R. LIDE, “CRC Handbooks of Chemistry and Physics” (CRC Press, Florida, 1994) p. 6.

Received 6 May
and accepted 21 August 2003