Asian Journal of Chemistry;   Vol. 23, No. 11 (2011), 4867-4870

ASIAN JOURNAL OF CHEMISTRY

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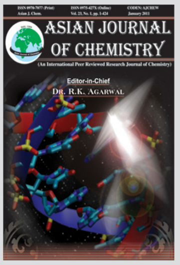

Solid-State Metathetic Synthesis of Ag-$ZnWO_4$/Zeolite-A: A Porous Composites Assisted by Microwave Irradiation

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(*Received*: 11 October 2010;   *Accepted*: 20 July 2011)   AJC-10168

Ag-$ZnWO_4$/zeolite-A porous composites were successfully synthesized from solid-state metathetic method using microwave irradiation. The wolframite-type $ZnWO_4$ has been synthesized where the characteristics of solid-state metathetic reaction and the formation of high lattice energy by-product NaCl drives the reaction toward completion. The Ag-$ZnWO_4$/zeolite-A porous composites were entirely completed at 600 °C. The monoclinic-like crystals of $ZnWO_4$ are primarily co-mixed with porous zeolite-A. The spherical small particles of silver are well immobilized in the porous $ZnWO_4$/zeolite-A matrix.

Key Words: Solid-state metathetic synthesis, Ag, $ZnWO_4$, Zeolite-A, Microwave irradiation.

INTRODUCTION

Metal tungstates with large radii of bivalent cations (*e.g.*, Ca, Ba, Pb and Sr) tend to Scheelite-type tetragonal structure, whilst small cationic radii (*e.g.*, Zn, Fe, Mn, Co and Ni) are favour of forming a Wolframite-type monoclinic structure. The main difference among the two above structures is that, every W atom is surrounded by four O atoms in a Scheelite-type structure, whilst six O atoms surround every W atom in MWO_4 tungstate crystallizing in a Wolframite-type structure. $ZnWO_4$ is a technologically important material with a monoclinic Wolframite-type structure in the space group P2/c. There are two formula units per primitive cell with lattice parameters[1] of $a = 4.69263$ Å, $b = 5.72129$ Å, $c = 4.92805$ Å and $\beta = 90.6321°$. The presence of two non-equivalent oxygen atoms is responsible for three pairs of Zn-O and W-O bonds, having different lengths. Thus both Zn nad W atoms are surrounded by six oxygens, forming distorted octahedral coordination.

In recent years $ZnWO_4$ has attracted considerable attention for potential applications as a scintillator, microwave devices, luminescent material and photocatalyst[2-7]. The physical, chemical and photochemical properties of $ZnWO_4$ were dependent on the manufacturing method. To enhance the applications of $ZnWO_4$, several processes have been developed over the last decade and can be classified. $ZnWO_4$ is prepared by a range of processes, such as the solid-state reaction method[8], co-precipitation method[9], molten salt[10], combustion[11], mechanochemical[12], sol-gel[13], hydrothermal reaction[14-18], citrate combustion[19], solvothermal[20] and metathetic approach[21].

Citrate combustion method[19], where several metal ions in a solution could be first chelated to form metal complexes and then polymerized to form a gel, seems to be most suitable among several chemical solution processes, because rigidly fixed cations are homogeneously dispersed in the polymer network and have few chances to segregate even during pyrolysis. However, in spite of the many advantages of the citrate combustion method, the weakness of the citrate combustion method is the difficulty of the effective removal of large amounts of organic substance. Based on this consideration, the citric acid complex as another chemical solution process was tried for the synthesis of $ZnWO_4$ nanopowders. There are several parameters for controlling the citric acid complex process to prepare $ZnWO_4$ particle with significant properties. Besides these established synthesis processes, finding simple and cost effective routes to synthesize $ZnWO_4$ is needed.

Microwave irradiation[19-21] as a heating method has found and developed a number of applications in chemistry and ceramic processing. Compared with the usual method, microwave synthesis has the advantages of very short reaction time, small particle size, narrow particle size distribution and high purity method in preparing nanocrystalline samples. Among these different methods the solution based chemical synthetic methods play a crucial role in the design and production of fine ceramics and have been successful in overcoming many of the limitations of the traditional solid-state, high-temperature methods. However, the use of solution chemistry can eliminate major problems such as long diffusion paths, impurities and agglomeration which result in products with improved homogeneity.

Wet chemical methods have disadvantages such as complicated synthetic steps, use of expensive equipment, high synthetic temperature and long sintering time. On the other hand, due to excessive energy consumption, complex apparatus and techniques the solid-state reaction becomes gradually unpopular and unsatisfied. However, solid-state synthesis of materials by metathetic route is simple method of synthesis, cost-effectiveness, high yield, easy scale up and emerging as a viable alternative approach to synthesize high-quality novel inorganic materials in a short amount of time. Solid state metathetic approach assisted by microwave irradiation has been successfully applied for the synthesis of metal tungstate of Wolframite-type MWO_4 (M = Zn, Mn, Ni) and Scheelite-type MWO_4 (M = Ca, Sr, Ba)[21]. The Ag incorporated $ZnWO_4$/zeolite-A porous composite are expected to have an excellent adsorption and synergy effects in an immobilization mechanism of metallic catalysts for the wide application such as sensors, photocatalysts, luminescence, antibacterial matrices and optical effect of wide range of UV and visible region.

In this study, the Ag-$ZnWO_4$/zeolite-A porous composites were synthesized from solid-state metathetic (SSM) method using microwave irradiation. The characteristics of solid-state metathetic reaction and the formation of high lattice energy by-product NaCl were discussed. The Ag-$ZnWO_4$/zeolite-A porous composites were immobilized from the mixed metathetic precursors to moderated temperatures. The synthesized Ag-$ZnWO_4$/zeolite-A porous composite powders were evaluated for the crystallization process, thermal decomposition and morphology.

EXPERIMENTAL

Fig. 1 shows a flow chart for synthesis of Ag-$ZnWO_4$/zeolite-A porous composites from the solid-state metathetic method using microwave irradiation. $ZnCl_2$ and $Na_2WO_4\cdot 2H_2O$ were used for the preparation of the metal tungstate compound. Preparation of zinc tungstate was carried out by reacting a well-ground mixture of $ZnCl_2$ and $Na_2WO_4\cdot 2H_2O$ in a molar ratio of 1:1. Sample mixtures were stirred at 60 °C for 3 h, after adding 2 wt % $AgNO_3$ and 5 wt % synthetic zeolite-A. The samples were dried at 100 °C overnight and put into crucibles and then exposed to domestic microwave operating (Samsung Electronic Corp. Korea) at a frequency of 2.45 GHz and a maximum out-put power of 1050 W for 10 min duration. The samples were washed with distilled water and ethanol many times to remove sodium chloride reaction by-product and dried at 80 °C on a hot plate. Heat-treatment of the samples was performed at 600 °C for 3 h.

The crystallization process of the samples was evaluated by thermogravimetry-differential thermal analysis (TG-DTA, Setram, France), using a sample weight of about 24 mg and a heating rate of 10 °C/min. The existing phase in the powders after heat-treatment was identified by ordinary X-ray diffraction (XRD, CuK_α, 40 kV, 30 mA, Rigaku, Japan) with a scan rate of 3 °/min. Fourier transform infrared spectroscopy (FT-IR, Model IR 550, Magna, Nicolet Company) was used for the interpretation of the thermal-decomposition behaviour of the metathetic reaction and heat-treated powders in frequency ranges from 4000-400 cm^{-1}. The FT-IR spectra were measured in KBr pellets. The microstructure and surface morphology of the nanocrystalline powders were observed by scanning electron microscopy (SEM, JSM-35CF, JEOL) and energy-dispersive X-ray detector(EDX).

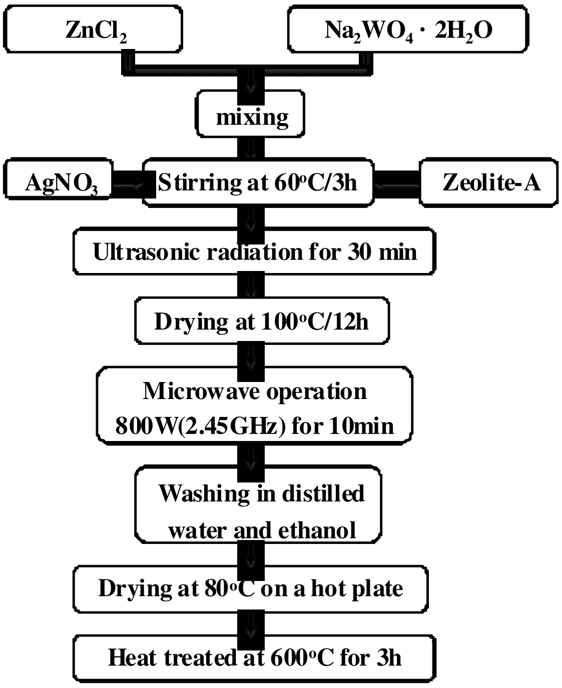

Fig. 1. Flow chart for synthesis of Ag-$ZnWO_4$/zeolite-A from the solid-state metathetic method using microwave irradiation

RESULTS AND DISCUSSION

The crystallization process of the $ZnWO_4$ was evaluated by DTA in Fig. 2. In Fig. 2, their combustion and crystallization of $ZnWO_4$ have been completed below 600 °C. No significant plateau, corresponding to well-defined intermediate products, appeared in the heating process. The DTA curve in Fig. 2 shows three exothermic peaks which could be further classified into two types of physical meaning: (1) left exothermic peak at 320 °C corresponds to initial decomposition of the precursor and (2) center exothermic peak at 365 °C and (3) right exothermic peaks at 552 °C correspond to the formation of the nucleus of the crystal and crystallization of $ZnWO_4$. Below 365 °C, the resultant powders were dark brown, hard and porous in structure, denoting an amorphous phase. It is attributed to contain a lot of carbons and ignitable organics. When the temperature further increases above 400 °C (just over 365 °C, the center exothermic peak), crystal nuclei begin to form and consequently the primary crystallizing process has been completed accompanying the combustion of the residual carbons and ignitable organics.

Fig. 3(a-e) shows the FT-IR spectra for the $ZnWO_4$ powders heated at 300-600 °C. For the precursor (Fig. 3(a)), the bands at 1620, 3445 cm^{-1} (O-H stretching modes), 1736, 1395 cm^{-1} (carboxyl group stretching modes), 1278 cm^{-1} (CH_3) and absorption bands near 877 cm^{-1} (W-O-Zn stretching mode) seem to define the relatively dehydrated (Zn·W)-citrate polymeric complex. Heat-treatment at 300 °C in Fig. 3(b) leads to

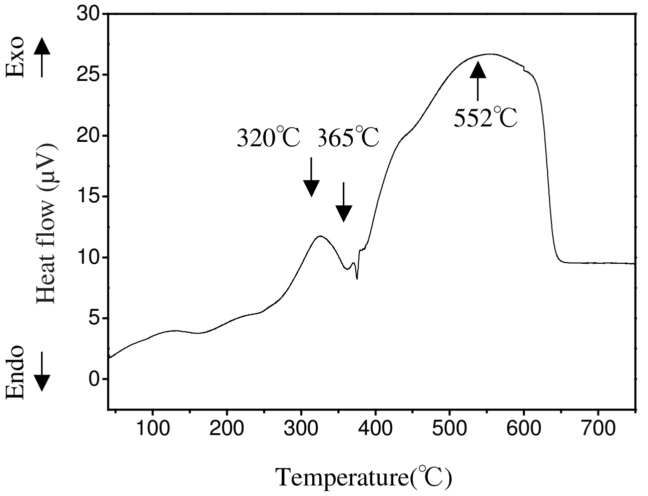

Fig. 2. DTA curves of the $ZnWO_4$

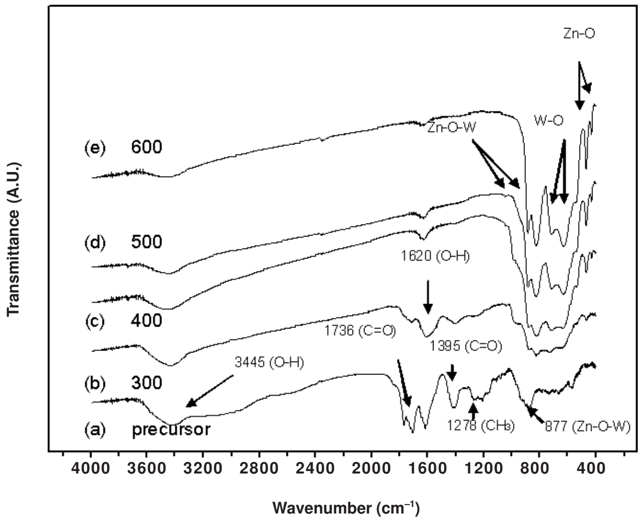

Fig. 3. FT-IR spectra of the $ZnWO_4$ heat-treated at 300-600 ºC for 3 h

a significant change in its infrared spectra. A decrease of the band at 1736, 1395 and 1620 cm^{-1} is produced, while the bands at 1278 cm^{-1} disappear. At 400 ºC in Fig. 3(c), the bands of the carbonyl group disappear, while new absorption bands appear between 900 and 400 cm^{-1}. In Fig. 3(c-e), the bending and stretching vibrations of Zn-O (532, 473 cm^{-1}), W-O (710, 633 cm^{-1}) and Zn-O-W bond (877, 834 cm^{-1}) could be identified to the synthesized $ZnWO_4$.

Fig. 4 shows XRD results for the phase identification of the Ag-$ZnWO_4$/zeolite-A porous composites heat-treated at 600 ºC for 3 h. The XRD patterns contain peaks corresponding to zinc tungstate and NaCl. The intensities of the peaks indicated higher intensity and confirmed the phases belong to Wolframite $ZnWO_4$. It is noted that the $ZnWO_4$ single phase could be observed at 600 ºC. The formation of NaCl as a by-product confirms the reaction is characteristic of solid state metathic reactions.

Fig. 5 shows a SEM micrograph of the $ZnWO_4$ synthesized by solid-state metathetic reaction showing the relatively exaggerated growth including rectangular elongated NaCl in the distributed $ZnWO_4$ powders, which was co-produced with high lattice energy. Parhi *et al.*[21] have established microwave metathetic synthesis of various metal tungstates, which has provided

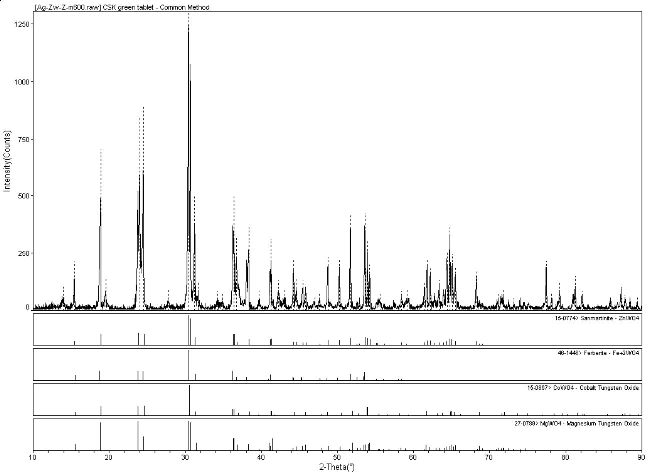

Fig. 4. XRD patterns of the Ag-$ZnWO_4$/zeolite-A porous composites heat-treated at (d) 600 ºC for 3 h

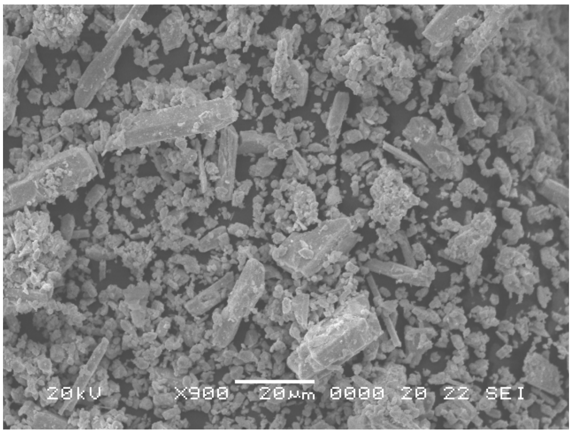

Fig. 5. A SEM micrograph of the ZnWO4 synthesized by SSM reaction showing elongated NaCl in distributed $ZnWO_4$ powders, which was co-produced with high lattice energy

the required energy to overcome the energy barrier which precludes spontaneous reaction and helped to heat the bulk of the material uniformly resulting in fine particles of controlled morphology and forming the product in a green manner without generation of any solvent wastes.

Solid state metathesis reactions, such as $ACl_2 + Na_2WO_4 \rightarrow AWO_4 + 2NaCl$, involves exchange of atomic/ionic species, where the driving force being the formation of thermodynamically stable alkali or alkaline earth halides with high lattice energy. Thermodynamic basis for such metathetic reactions are reported in the literature[21-24]. Parhi *et al.*[21], calculated the enthalpy (ΔH) and free energy change (ΔG) associated with the formation of tungstates and presented the result of ΔH -36.17 KJ/mol for $ZnWO_4$ that both enthalpy change favours the metathesis reaction and the enthalpy change is indeed the driving force for the metathesis involving the formation of NaCl. Solid-state metathetic reactions occur so rapidly that all of the released enthalpy is essentially used to heat up the solid products, usually raising the alkali halide near or above its normal boiling point and have been recognized as approximately adiabatic in nature[25].

The samples are washed with distilled water and ethanol to dissolve NaCl. Fig. 6 shows a SEM micrograph of the $ZnWO_4$ synthesized by solid-state metathetic reaction after

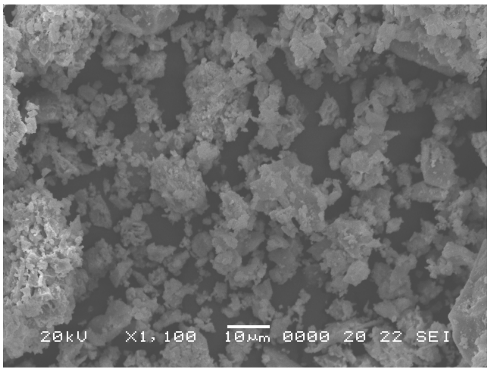

Fig. 6. A SEM micrograph of the $ZnWO_4$ synthesized by solid-state metathetic reaction after removing the NaCl

removing the NaCl, zinc tungstate crystallizes in wolframite crystal structure. Presence of sodium chloride confirms the reaction has proceeded in solid-state metathesis way. Fig. 7 shows a SEM micrograph of Ag-$ZnWO_4$/zeolite-A porous composites at 600 ºC for 3 h. The composite powders at 600 ºC shows co-mixed morphology. The monoclinic-like crystals of $ZnWO_4$ are primarily co-mixed with porous zeolite-A. The spherical small particles of silver are well immobilized in the porous $ZnWO_4$/zeolite-A matrix. Fig. 8 shows EDX patterns (a), SEM image (b) and quantitative results (c) of the synthesized Ag-$ZnWO_4$/zeolite-A porous composites at 600 ºC for 3 h. The quantitative results of the morphology are composed of Ag, $ZnWO_4$, zeolite-A.

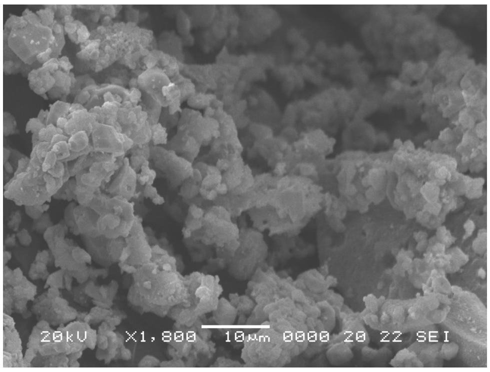

Fig. 7. A SEM micrograph of Ag-$ZnWO_4$/zeolite-A at 600 ºC for 3 h

For tungstate materials to be used as practical applications, the versatile characteristics is required for the particle size distribution and morphology of the particles. The well-defined particle features of the Ag-$ZnWO_4$/zeolite-A porous composites synthesized by solid-state metathetic reactions have control over morphology of the final particles and could be used for such technological application. Due to the enthalpy change by the driving force for the metathetic formation of NaCl, the SSM reactions affect not only the morphology of the particles of $ZnWO_4$, but also the formation of functional zeolite as well as the immobilized Ag in porous composite matrix. Therefore, the variation of metathetic reactions of $ZnCl_2 + Na_2WO_4 \rightarrow ZnWO_4 + 2NaCl$ are required for the control of the well-defined particle features of the Ag-$ZnWO_4$/zeolite-A porous composite. In the near future, the solid solution of the $Zn_xFe_{1-x}WO_4$ will be prepared and varied of the metathetic reactions with different driving forces showing the control of the morphology of the Ag- $Zn_xFe_{1-x}WO_4$/zeolite-A porous composites.

Conclusion

Ag-$ZnWO_4$/zeolite-A porous composites were successfully synthesized from solid-state metathetic method using microwave irradiation. The Ag-$ZnWO_4$/zeolite-A porous composites at 600 ºC for 3 h were entirely completed at a temperature of 600 ºC. The NaCl as a by-product by solid-state metathetic reaction showed the relatively exaggerated growth including rectangular elongated morphology in the distributed $ZnWO_4$ powders, which was co-produced with high lattice energy. The monoclinic-like crystals of $ZnWO_4$ are primarily co-mixed with porous zeolite-A. The spherical small particles of silver are well immobilized in the porous $ZnWO_4$/zeolite-A matrix.

ACKNOWLEDGEMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology (2010-0023911).

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