

Preparation and characterization of Ag incorporated ZnWO₄/zeolite composites by cyclic microwave metathetic method

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A solid-state metathetic (SSM) route assisted by cyclic microwave irradiation was used to synthesize the Ag incorporated ZnWO₄/zeolite composites under environmentally friendly conditions. The crystallized Ag incorporated ZnWO₄/zeolite composites were formed at 600 °C for 3 h, showing a well immobilized morphology with sizes of 3–5 μm. The synthesized Ag incorporated ZnWO₄/zeolite composites were characterized by scanning electron microscopy, energy-dispersed X-ray spectroscopy and Fourier transform infrared spectroscopy. Monoclinic-like crystals of ZnWO₄ were primarily co-mixed with zeolite. Small spherical silver particles were immobilized in the ZnWO₄/zeolite matrix.

Key words: Solid-state metathetic synthesis, Ag, ZnWO₄, Zeolite-A, Cyclic microwave irradiation.

Introduction

Metal tungstates with large bivalent cations (e.g., Ca, Ba, Pb, and Sr) tend to have a scheelite-type tetragonal structure, whereas small cationic radii (e.g., Zn, Fe, Mn, Co, and Ni) favor the formation of a wolframite-type monoclinic structure. The main difference between the above two structures is that every W atom is surrounded by four O atoms in a scheelite-type structure, whereas six O atoms surround every W atom in MWO₄ tungstate crystallizing in the wolframite-type structure. ZnWO₄ 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 of $a = 4.69263 \text{ \AA}$, $b = 5.72129 \text{ \AA}$, $c = 4.92805 \text{ \AA}$ and $\beta = 90.6321^\circ$ [1]. The presence of two non-equivalent oxygen atoms is responsible for three pairs of Zn-O and W-O bonds with different lengths. Therefore, both Zn and W atoms are surrounded by six oxygen atoms, forming a distorted octahedral coordination.

In recent years, ZnWO₄ has attracted considerable attention for potential applications as a scintillator, luminescent material and photocatalyst and microwave devices [2–7]. The physical, chemical and photochemical properties of ZnWO₄ are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of ZnWO₄. ZnWO₄ is prepared by a range of processes, such as solid-state reactions [8], co-precipitation [9], molten salt [10], combustion [11], mechano-chemical [12] sol-gel [13], hydrothermal reaction

[14–16, 20, 21], Microwave assisted synthesis [17–19].

Microwave assisted synthesis [17–19], as a heating method, has a number of applications in chemistry and ceramic processing. Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, small particle size, narrow particle size distribution, and a high purity method for preparing polycrystalline samples. Microwave heating is delivered to the surface of the material by radiant and/or convection heating, which is transferred to the bulk of the material via conduction. Microwave energy is delivered directly to the material through molecular interactions with an electromagnetic field. Heat can be generated through volumetric heating because microwaves can penetrate the material and supply energy. Wet chemical methods have disadvantages, such as complicated synthetic steps, the use of expensive equipment, high synthetic temperature and long sintering times. On the other hand, the solid-state reaction requires complex apparatus and techniques, which are becoming gradually unpopular due to excessive energy consumption. However, solid-state synthesis of materials by the metathetic route is a simple method of synthesis, which is cost-effective, gives a high yield and easy scale up, and is emerging as a viable alternative approach for synthesizing high-quality novel inorganic materials in a short time.

Ag-incorporated ZnWO₄/zeolite-A porous composites are expected to have excellent adsorption and synergy effects in an immobilization mechanism of metallic catalysts for a wide range of applications, such as sensors, photocatalysts, luminescence, anti-bacterial matrices, and optical effects in the UV and visible region. However, the study of microwave-assisted synthesis Ag incorporated ZnWO₄/zeolite composites by cyclic microwave metathetic reaction has not been published previously. In this study, Ag incorporated ZnWO₄/zeolite composites were synthesized using

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a solid-state metathetic (SSM) method with cyclic microwave irradiation. The characteristics of the SSM reaction of Ag incorporated ZnWO₄/zeolite composites are discussed in detail based on the formation of a high lattice energy by-product of NaCl. The synthesized Ag incorporated ZnWO₄/zeolite composites were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR).

Experimental

Fig. 1 shows a flow chart for the synthesis of Ag-ZnWO₄/zeolite composites by the solid-state metathetic method using cyclic microwave irradiation. ZnCl₂ and Na₂WO₄·2H₂O of analytic reagent grade were used to prepare the metal tungstate compound. The preparation of zinc tungstate was carried out by reacting a well-ground mixture of ZnCl₂ and Na₂WO₄·2H₂O at a molar ratio of 1 : 1. The sample mixtures were dried at 100 °C for 12 h, and 5 wt% AgNO₃ and 25 wt% synthetic zeolite-A were then added. The samples were placed into crucibles and exposed to domestic microwave (Samsung Electronics Corp. Korea) operating at a frequency of 2.45 GHz and a maximum out-put power of 1250 W. The cyclic microwave operation was set between 60 seconds on and 30 seconds off for 15 minutes. The samples were treated with ultrasonic radiation and washed many times with distilled water and ethanol to remove the sodium chloride reaction by-product. The samples were dried at 100 °C in an oven. Heat-treatment of the samples was performed at 600 °C for 3 h.

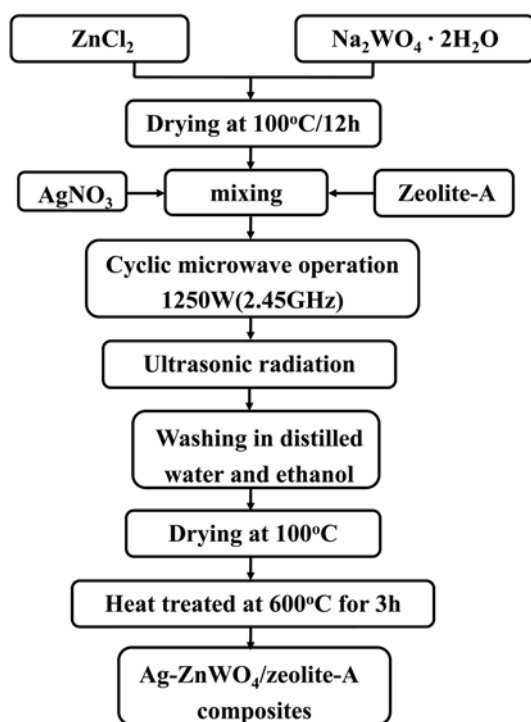


Fig. 1. Flow chart for the synthesis of Ag-ZnWO₄/zeolite composites by the SSM method using cyclic microwave irradiation.

Fourier transform infrared spectroscopy (FT-IR, Model IR 550, Magna, Nicolet Company) was used to examine the thermal-decomposition behavior of the cyclic metathetic reaction and heat-treated powders over a frequency range, 400 to 4,000 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 spectroscopy (EDS).

Results and Discussion

Fig. 2 shows FT-IR spectra of the Ag-ZnWO₄/zeolite composites after (a) cyclic microwave metathetic reaction (Ag-ZnW-Z-m) and (b) heat treated at 600 °C for 3 h (Ag-ZnW-Z-m600). The absorption bands at 473 and 530 cm⁻¹ can be assigned to the symmetric and asymmetric deformation mode of Zn-O in ZnO₆ octahedra. The absorption bands with their maxima at 633 and 710 cm⁻¹ can be due to the stretching modes of W-O in WO₆ octahedra. The bands at 834 and 877 cm⁻¹ were due to symmetrical vibrations of bridging oxygen atoms of the Zn-O-W groups. These vibrations could be identified to be from the synthesized ZnWO₄. The band at 1630 cm⁻¹ can in Fig. 3(a) Ag-ZnW-Z-m be assigned to HOH bending vibrations. It is assumed that the samples prepared contain a significant amount of surface-adsorbed water and alcohol.

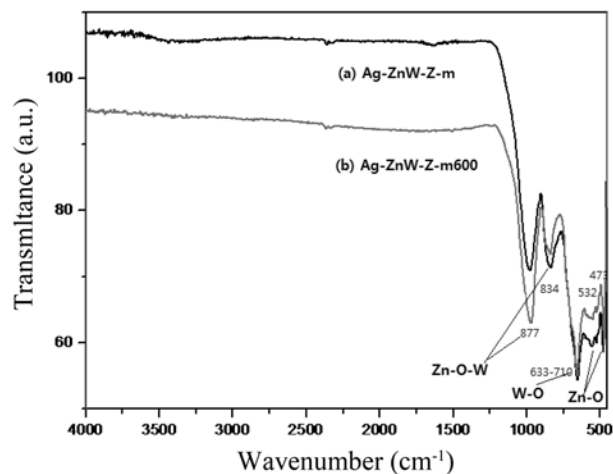


Fig. 2. FT-IR spectra of the Ag-ZnWO₄/zeolite composites after (a) cyclic microwave metathetic reaction (Ag-ZnW-Z-m) and (b) heat treated at 600 °C for 3 h (Ag-ZnW-Z-m600).

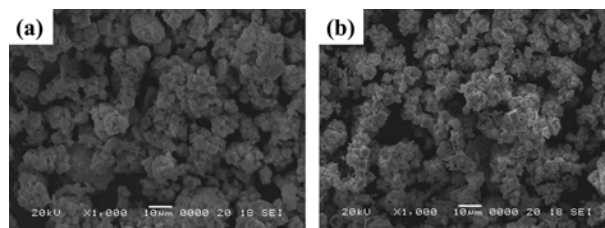


Fig. 3. SEM images of Ag-ZnWO₄/zeolite composites after (a) cyclic microwave metathetic reaction and (b) heat treated at 600 °C for 3 h.

Obviously, the bands at 1630 cm^{-1} disappeared after the heat treatment at $600\text{ }^{\circ}\text{C}$ for 3 h in Fig. 3(b) Ag-ZnW-Z-m600.

Fig. 3 shows SEM images of Ag-ZnWO₄/zeolite composites after (a) cyclic microwave metathetic reaction and (b) heat treated at $600\text{ }^{\circ}\text{C}$ for 3 h. The cyclic microwave metathetic synthesis resulted in the homogeneous morphology with sizes of $3\text{--}5\text{ }\mu\text{m}$ in Fig. 3(b). The monoclinic-like crystals of ZnWO₄ were primarily co-mixed with zeolite. The spherical small particles of silver were well immobilized in the porous ZnWO₄/zeolite matrix. The Ag incorporated ZnWO₄/zeolite composites were well synthesized in a green manner without the generation of solvent waste, because the cyclic microwave radiation provided the energy required to overcome the energy barrier. It helped to heat the bulk of the material uniformly resulting in fine particles with a controlled morphology, and to fabricate the product in a green manner without the generation of solvent waste. The solid state metathesis reaction, such as $\text{ZnCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{ZnWO}_4 + 2\text{NaCl}$, involves the exchange of atomic/ionic species, where the driving force is the formation of a thermodynamically-stable alkali or alkaline earth halide with high lattice energy [26, 27]. The

enthalpy change favors the metathesis reaction and is the driving force accompanying the formation of NaCl [19, 28]. SSM reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products. The solid-state metathesis reactions assisted by cyclic microwave irradiation provide convenient route for the synthesis of the Ag incorporated ZnWO₄/zeolite composites, which were obtained in the form of loosely connected micron sized particles at considerably lower temperatures than those usually employed for their synthesis. For the Ag incorporated ZnWO₄/zeolite composites materials to be used for practical applications, control of the particle size distribution and morphology of the particles is needed. The well-defined particle features of the Ag incorporated ZnWO₄/zeolite composites synthesized by SSM reactions assisted by cyclic microwave irradiation have control over the morphology of the final particles, and can be used for such technological applications.

Fig. 4 shows (a) an EDS pattern, (b) a SEM image, and (c) quantitative results of the synthesized Ag-ZnWO₄/zeolite composites synthesized at $600\text{ }^{\circ}\text{C}$ for 3 h. The quantitative compositions in Table 1 of the synthesized Ag-ZnWO₄/zeolite composites are seen to be composed

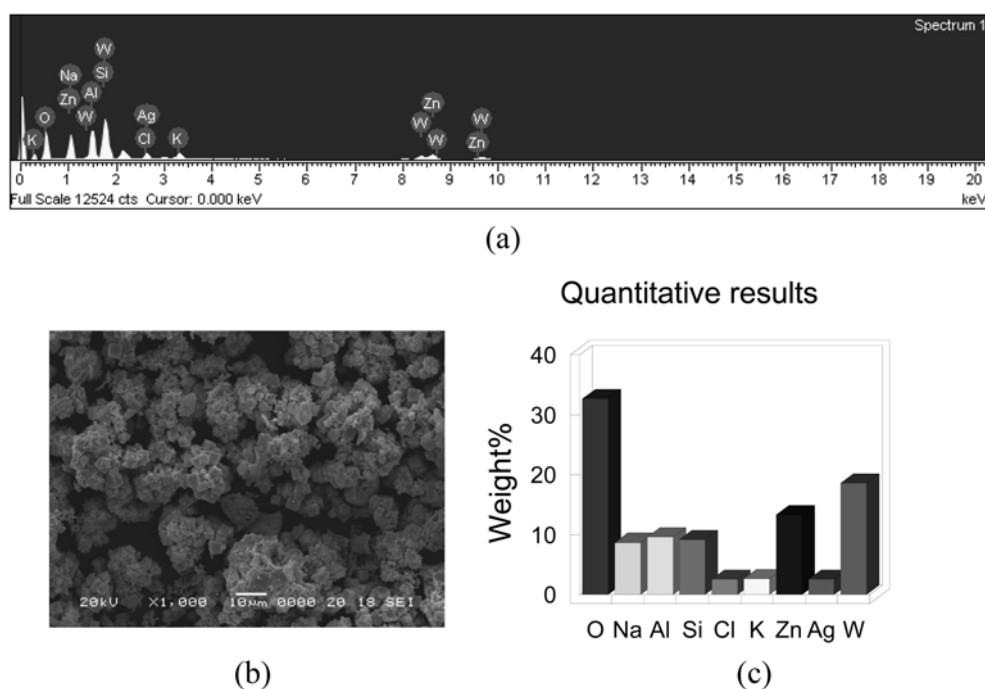


Fig. 4. EDS pattern (a), SEM image (b), and quantitative results (c) of the Ag-ZnWO₄/zeolite composites synthesized at $600\text{ }^{\circ}\text{C}$ for 3 h.

Table 1. Quantitative compositions(wt%) of the Ag-ZnWO₄/zeolite composites synthesized at $600\text{ }^{\circ}\text{C}$ for 3 h

Spectrum	In stats.	O	Na	Al	Si	Cl	K	Zn	Ag	W	Total
Spectrum1	Yes	32.73	8.71	9.60	9.17	2.58	2.65	13.29	2.62	18.64	100.00
Mean		32.73	8.71	9.60	9.17	2.58	2.65	13.29	2.62	18.64	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.		32.73	8.71	9.60	9.17	2.58	2.65	13.29	2.62	18.64	
Min.		32.73	8.71	9.60	9.17	2.58	2.65	13.29	2.62	18.64	

of Ag, ZnWO₄ and zeolite. For tungstate materials to be used for practical applications, versatile characteristics are required for the particle size distribution and morphology of the particles. The well-defined particle features of the Ag-ZnWO₄/zeolite composites synthesized by SSM reactions assisted by the cyclic microwave irradiation give control over the morphology of the final particles, and can be used for such technological applications. Owing to the enthalpy change by the driving force for the metathetic formation of NaCl, the SSM reactions affect not only the morphology of the ZnWO₄ particles, but also the formation of functional zeolite and Ag immobilized in the composite matrix. Therefore, a variation of metathetic reactions of $\text{ZnCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{ZnWO}_4 + 2\text{NaCl}$ is required to control the well-defined particle features of the Ag-ZnWO₄/zeolite-A composites.

Conclusions

Ag-ZnWO₄/zeolite-A porous composites were synthesized using a solid-state metathetic method with cyclic microwave irradiation. The Ag-ZnWO₄/zeolite composites synthesized at 600 °C for 3 h were completed entirely. The absorption bands of FTIR at 473 and 530 cm⁻¹ can be assigned to the symmetric and asymmetric deformation mode of Zn-O in ZnO₆ octahedra. The absorption bands with their maxima at 633 and 710 cm⁻¹ can be due to the stretching modes of W-O in WO₆ octahedra. The bands at 834 and 877 cm⁻¹ were due to symmetrical vibrations of bridging oxygen atoms of the Zn-O-W groups. The cyclic microwave metathetic synthesis resulted in the homogeneous morphology with sizes of 3-5 μm. The monoclinic-like crystals of ZnWO₄ were primarily co-mixed with zeolite. The spherical small particles of silver were well immobilized in the ZnWO₄/zeolite matrix. The Ag incorporated ZnWO₄/zeolite composites were well synthesized in a green manner without the generation of solvent waste.

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