Asian Journal of Chemistry; Vol. 25, No. 5 (2013), 2359-2362

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.12636B

Preparation and Characterization of Ag Incorperarted $MnWO_4$/Zeolite Composites by Microwave-Assisted Metathetic Reaction

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(*Received*: 2 November 2011; *Accepted*: 5 November 2012) AJC-12359

Ag-$MnWO_4$/zeolite-A porous composites were synthesized using a solid-state metathetic method with microwave irradiation. The characteristics of the solid-state metathetic reaction and the formation of by-product NaCl were found to drive the reaction for wolframite-type $MnWO_4$ toward completion. The Ag-$MnWO_4$/zeolite-A porous composites were formed completely at 600 ºC. Monoclinic-like crystals of $MnWO_4$ were primarily co-mixed with porous zeolite-A. Small spherical silver particles were immobilized in the porous $MnWO_4$/zeolite-A matrix.

Key Words: Solid-state metathetic synthesis, Ag-$MnWO_4$/zeolite-A porous composite, Microwave irradiation.

INTRODUCTION

Metal tungstates has attracted extensive attention because of their particular importance in investigating the sizes and shape-dependent properties as well as their immobilization in porous materials for potential applications. 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-$MnWO_4$/zeolite-A porous composites are required for the immobilization features for the potential applications[1-7].

During past years, various processes have been developed to enhance the applications of metal tungstates are prepared by a range of processes, such as a solid-state reaction[8,9], co-precipitation[10-12], a molten salt method[13,14], a hydrothermal reaction[15,16], a combustion method[17], a mechano-chemical method[18], from a polymeric precursor[19], by microwave irradiations[20-22]. The microwave synthesis has the advantages of a very short reaction time, small particle size, narrow particle size distribution and high purity method for preparing polycrystalline samples. Solid-state synthesis of materials by the metathetic route is a simple method of synthesis, cost-effective, 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[23,24]. The solid state metathetic approach assisted by microwave irradiation has been applied successfully to the synthesis of metal tungstate of wolframite-type metal tungstates[25-29]. Silver-incorporated $MnWO_4$/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, antibacterial matrices and optical effects in the UV and visible region.

In this study, Ag-$MnWO_4$/zeolite-A porous composites were synthesized using a solid-state metathetic method with microwave irradiation. The characteristics of the solid-state metathetic reaction and the formation of by-product NaCl were discussed. The Ag-$MnWO_4$/zeolite-A porous composites were immobilized from mixed metathetic precursors at moderate temperatures. The crystallization process, thermal decomposition and morphology of the synthesized Ag-$MnWO_4$/zeolite-A porous composite powders were evaluated.

EXPERIMENTAL

Fig. 1 shows a flow chart for the synthesis of Ag-$MnWO_4$/zeolite-A porous composites from the solid-state metathetic method using microwave irradiation. $MnCl_2 \cdot 4H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were used to prepare the metal tungstate compound. The preparation of metal tungstates were carried out by reacting well-ground mixtures of $MnCl_2 \cdot 4H_2O$ and $Na_2WO_4 \cdot 2H_2O$ for $MnWO_4$ at a molar ratio of 1:1. The sample mixtures were dried at 100 ºC for 12 h and 5 wt % $AgNO_3$ 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 for 10 min. The samples were treated with ultrasonic radiation and washed many times with distilled water and ethanol to remove

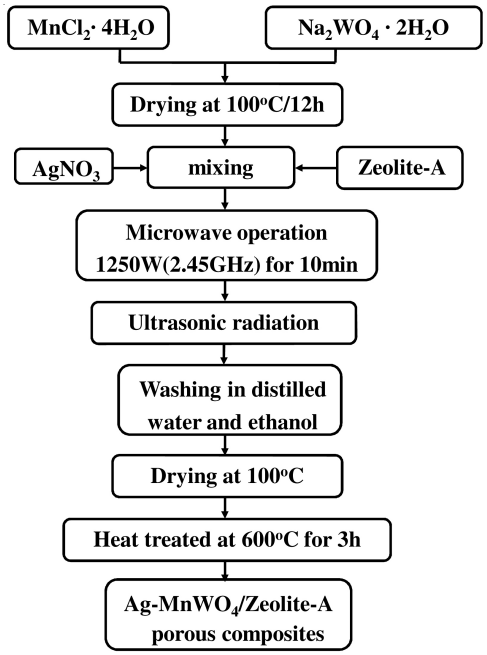


Fig. 1. Flow chart for the synthesis of Ag-$MnWO_4$/zeolite-A porous composites from the SSM method using microwave irradiation

the sodium chloride reaction by-product. The samples were dried at 100 ºC in an oven. Heat-treatment of the samples was performed at 600 ºC for 3 h.

The phase existings in the particles after the solid-state metathetic reactions and heat-treatment were identified by XRD (D/MAX 2200, Rigaku, Japan). FTIR (Nicolet IR200, Thermo Electron corporation, USA) was used to examine the thermal-decomposition behaviour of the solid-state metathetic reaction and the obtained particles over the frequency range, 4000 to 400 cm^{-1}. The microstructure and surface morphology of the Ag-$MnWO_4$/zeolite-A porous composite powders were observed by scanning electron microscopy (JSM-5600, JEOL, Japan) and energy-dispersive X-ray spectroscopy (EDS).

RESULTS AND DISCUSSION

Fig. 2 shows FT-IR spectrum of the Ag-$MnWO_4$/zeolite-A porous composites after (a) solid-state metathetic reaction (Ag-$MnWO_4$-Z-m) and (b) heat-treatment at 600 ºC for 3 h (Ag-$MnWO_4$-Z-m600). The absorption bands at 473 and 532 cm^{-1} can be assigned to symmetric and asymmetric deformation mode of Mn-O in MnO_6 octahedra. The absorption bands with their maxima at 633 and 710 cm^{-1} can be due to the stretching modes of W-O in WO_6 octahedra. The bands at 834 and 877 cm^{-1} were due to symmetrical vibrations of bridge oxygen atoms of the Mn-O-W groups.

Fig. 3 shows SEM images of the Ag-$MnWO_4$/zeolite-A porous composites after (a)/(b) solid-state metathetic reaction and (c)/(d) heat-treatment at 600 ºC for 3 h. Fig. 3(a) and (b) shows SEM images of the Ag-$MnWO_4$/zeolite-A porous composites synthesized by solid-state metathetic reaction after removing the NaCl. $MnWO_4$ crystallizes in wolframite crystal structures. Presence of sodium chloride confirms the reaction has proceeded in solid-state metathesis way. Parhi *et al.*[25] reported the microwave metathetic synthesis of various

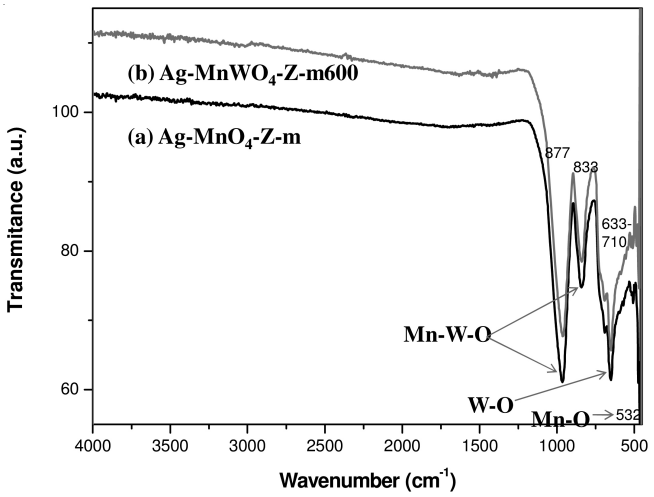


Fig. 2. FT-IR spectra of the Ag-$MnWO_4$/zeolite-A porous composites after (a) solid-state metathetic reaction and (b) heat-treatment at 600 ºC for 3 h

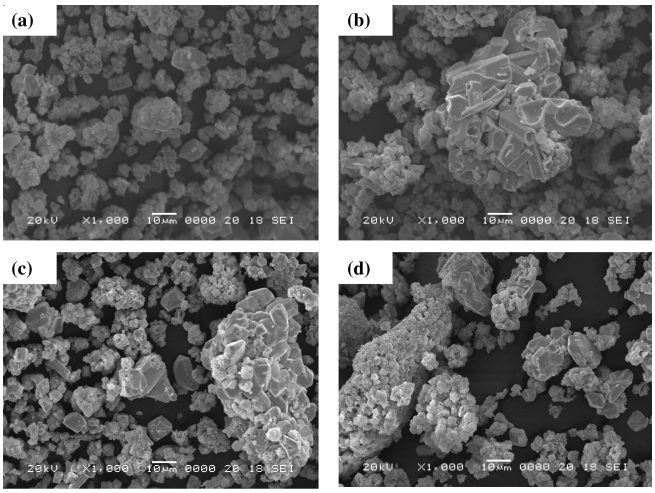
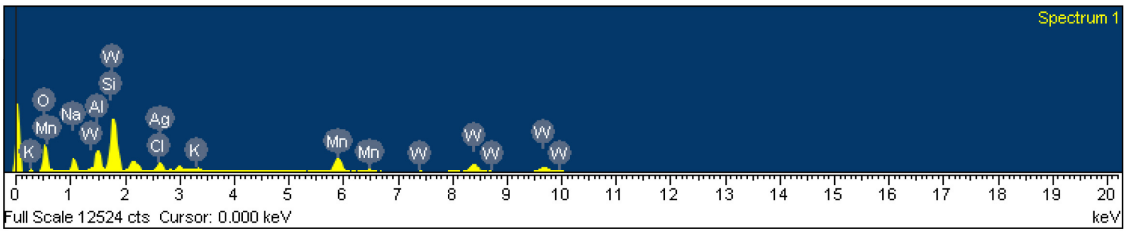


Fig. 3. SEM images of the Ag-$MnWO_4$/zeolite-A porous composites after (a) and (b) solid-state metathetic reaction and (c) and (d) heat-treatment at 600 ºC for 3 h

metal tungstates and showed that microwave radiation provided the energy required to overcome the energy barrier that precludes a spontaneous reaction and helped heat the bulk of the material uniformly, resulting in fine particles with a controlled morphology and the formation of the product in a green manner without the generation of solvent waste.

In Fig. 3 (c) and (d), the SEM images of Ag-$MnWO_4$/zeolite-A porous composites after solid-state metathetic reaction and followed by heat-treatment at 600 ºC for 3 h show the well crystallized $MnWO_4$ on the zeolite-A synthesized by a solid-state metathetic reaction. The monoclinic-like crystals of $MnWO_4$ were primarily co-mixed with Ag on the porous zeolite-A surfaces. The spherical small particles of silver were well immobilized in the porous $MnWO_4$/zeolite-A composites matrix. Solid state metathesis reactions, such as $MnCl_2 + Na_2WO_4 \rightarrow MnWO_4 + 2NaCl$, involves the exchange of atomic/ionic species, where the driving force is the formation of thermodynamically stable alkali or alkaline earth halides with high lattice energy. The thermodynamic basis for such metathetic reactions has been reported[25,30-32]. Parhi *et al.*[24]

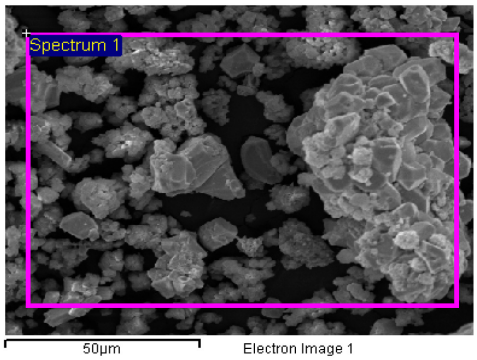
(a)



(b)

Spectrum	In stats.	O	Na	Al	Si	Cl	K	Mn	Ag	W	Total
Spectrum 1	Yes	30.46	6.11	5.50	4.94	3.25	0.88	11.95	4.71	32.21	100.00
Mean		30.46	6.11	5.50	4.94	3.25	0.88	11.95	4.71	32.21	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.		30.46	6.11	5.50	4.94	3.25	0.88	11.95	4.71	32.21	
Min.		30.46	6.11	5.50	4.94	3.25	0.88	11.95	4.71	32.21	

(c)



(d)

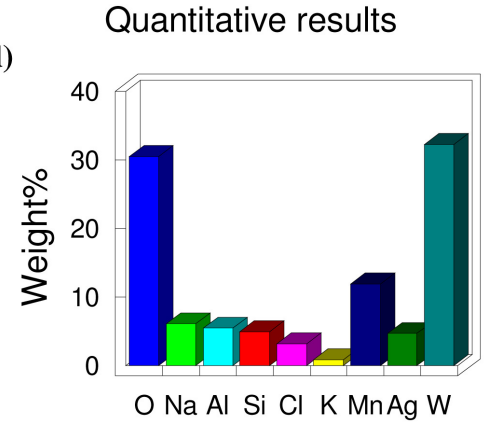


Fig. 4. EDS patterns (a), quantitative compositions (b), a SEM image (c) and quantitative results (d) of the synthesized Ag-$MnWO_4$/zeolite-A porous composites

calculated the enthalpy (ΔH) and free energy change (ΔG) associated with the formation of tungstates and reported ΔH = -36.17 KJ/mol for $MnWO_4$ showing that both the 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 the enthalpy released 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 to be approximately adiabatic in nature[33].

Fig. 4 shows (a) EDS patterns, (b) quantitative compositions, (c) a SEM image and (d) quantitative results of the synthesized Ag-$MnWO_4$/zeolite-A porous composites at 600 ºC for 3 h. The EDS patterns and quantitative compositions of the synthesized Ag-$MnWO_4$/zeolite-A porous composites were composed of Ag, $MnWO_4$ and zeolite-A. Fig. 4 shows (a) EDS patterns, (b) quantitative compositions, (c) a SEM image and (d) quantitative results of the synthesized Ag-$MnWO_4$/zeolite-A porous composites at 600 ºC for 3 h. The EDS patterns and quantitative compositions of the synthesized Ag-$MnWO_4$/zeolite-A porous composites were composed of Ag, $MnWO_4$ and zeolite-A.

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-$MnWO_4$/zeolite-A porous composites synthesized by solid-state metathetic reactions have 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 solid-state metathetic reactions affect not only the morphology of the $MnWO_4$ particles, but also the formation of functional zeolite and Ag immobilized in the porous composite matrix. Therefore, a variation of metathetic reactions of $MnCl_2 + Na_2WO_4 \rightarrow MnWO_4 + 2NaCl$ is required to control the well-defined particle features of the Ag-$MnWO_4$/zeolite-A porous composites.

Conclusion

Ag-$MnWO_4$/zeolite-A porous composites were synthesized using solid-state metathetic method with microwave irradiation. The Ag-$MnWO_4$/zeolite-A porous composites at 600 ºC for 3 h were completed entirely at 600 ºC. The well crystallized $MnWO_4$ on the zeolite-A synthesized by a solid-state metathetic reaction. The monoclinic-like crystals of $MnWO_4$ were primarily co-mixed with Ag on the porous zeolite-A surfaces. The spherical small particles of silver were well immobilized in the porous $MnWO_4$/zeolite-A composites matrix. The 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 the enthalpy released is essentially used to heat up the solid products of Ag-$MnWO_4$/zeolite-A porous composites.

ACKNOWLEDGEMENTS

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012-0007858).

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