In situ solid phase microwave assisted synthesis of silver/nickel substituted phosphomolybdate nanoparticles using organic driving agent

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Abstract: A solid state microwave assisted technique was used for facile and eco-friendly synthesis of silver/nickel substituted salt of phosphomolybdate nanoparticles. This solid phase reaction was promoted using urea as organic driving agent under microwave treatment with the power of 360 W for 7 min. The structural and morphological characterizations revealed the formation of mixed silver/nickel ammonium salt of phosphomolybdate with Keggin-type structure and uniform nano-sized particulate morphology with the average size about 41 nm. The experimental strong point of this strategy is the use of a facile, one-pot and solid state method for synthesis of nanomaterials at short time without any acidic conditions. As a result, this method can be proposed as an instrumental way to fabricate various macromolecules of polyoxometalate in nanoscale.

Keywords: Solid state microwave, Nanoparticles, Polyoxometalate, Organic driving agent.

Introduction

Polyoxometalates (POMs) with a Keggin structure are a well-known class of mixed metal oxides due to their special properties and potential applications in materials science, gas sensing, bioscience, medicine, catalysis [1-5]. Although these polyanion compounds are introduced as the effective materials in various applications, their wide practical uses have been hindered by their low structural stability, multi-stage complex synthesis methods and poor reproducibility. The substitution and incorporation of different counter cations in these molecules and production of their salts is one of the solutions to overcome the mentioned weaknesses, which yields a versatile manner in these compounds [6-8]. In fact, the nature of cationic unit effects on the chemical and physical properties of POMs. Therefore, the design of POM molecules can be developed based on the different kinds of substituted counter cations [7-9]. Due to fact-growing demand for the application of such compounds, introduction of a simple, safe, low cost and high efficient synthesis strategy has favored. The most of the described synthesis methods in literature for the preparation of POMs require to severe acidic experimental conditions and complex equipment [10-14]. Among the reported methods solid state microwave assisted technique is an interesting method. It is a simple, cost effective, environmental friendly and rapid method to synthesize materials in micro and nano scales. In this technique, the heating energy resulting from the reactant-microwave interactions leads to prepare the product at short reaction time. In addition, the use of effective organic reagents can accelerate the reaction and create the suitable conditions to produce nano-sized architectures [15]. The use of organic driving agents such as urea promote the synthesis reaction and also, act as capping agent for the trapping of metal units in specific orientations to provide an appropriate morphology of product [16, 17]. To the best of our knowledge, the preparation of mixed ammonium salts of phosphomolybdate polyoxoanion in nano-sized particles by solid state microwave assisted strategy using urea as driving agent has not been yet reported. The present work reports a facile and rapid microwave assisted strategy for synthesis of the substituted Ag^+/Ni^{2+} ammonium salts of phosphomybdate nanoparticles. The product was characterized by FT-IR, XRD, EDX and SEM techniques.

Experimental

Materials and synthesis method

All chemicals were purchased from Merck Co. and used without further purification. To prepare product, the stoichiometric amounts of metal nitrate salts were mixed to each other in the presence of urea and ammonium nitrate as driving agents in solid phase. The mixture was transferred into a domestic microwave oven with a power of 360 W for 7 min. The yellow colored powder was obtained and analyzed by FT-IR, XRD, SEM and EDX techniques.

Characterizations

The X-ray diffraction (XRD) patterns were recorded by a STOE powder diffraction system using CuKα radiation (wavelength, λ=1.54060 Å). Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy analysis (EDX) were taken on VEGA\TESCAN S360 with gold coating.

Results and Discussion

Fig. 1 indicates FT-IR spectrum of the prepared mixed ammonium polyoxoanion after solid state microwave heating reaction using urea with a power of 360 W for 7 min. The appeared peaks especially in low wavenumber range of 1100–500 cm^{-1} indicate the formation of ammonium molybdophosphate compound with a Keggin-type structure [18]. The observed peaks at 1062, 962, 864 and 788 cm^{-1} are attributed to the asymmetric stretching vibrations of P–O_a, Mo–O_d, Mo–O_b–Mo, Mo–O_c–Mo, respectively. The marked oxygen atoms of O_a, O_b, O_c and O_d refer to the constitutive oxygen atoms of the Keggin structure; O_a indicates the O atom shared between PO_4 tetrahedron and a trimetallic group, O_b is the oxygen atom linking two trimetallic groups, O_c is the O atom linking two MoO_6 octahedral group inside a trimetallic unit and O_d refers to the terminal oxygen atom of this structure. The characteristic band at 595 cm^{-1} can be related to the P-O bending vibration frequency [7, 18]. The peaks at 1413, 1625 and 3207 cm^{-1} are assigned to the vibration frequencies of ammonium ions and H_2O molecules, respectively [7, 19]. Since it is observed no significant difference between

NH_4PMo_{12} FT-IR spectrum (shown in the inset of Fig. 1.) and that of $XPMo_{12}$ salt, it can be concluded that the primary Keggin structure has been remained and only the ammonium ions have been partially substituted by X ions.

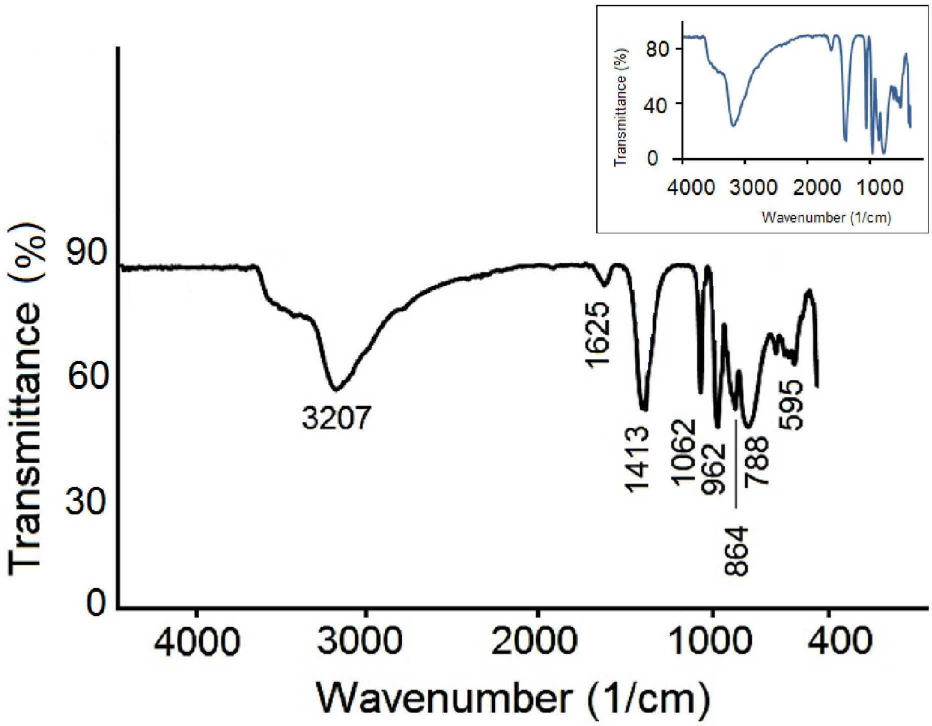

Fig. 1. FT-IR spectrum of the prepared ammonium silver/nickel phosphomolybdate nanoparticles, $AgNiPMo_{12}$, FT-IR spectrum of NH_4PMo_{12} is shown in the inset of this Fig.

The recorded XRD pattern of the resulting product demonstrated the formation of $(NH_4)_3PMo_{12}O_{40}.xH_2O$ phase with a high crystallinity. It represents that the employed X ions (X= Ag^+ and Ni^{2+}) have occupied counter-ion positions in the obtained polyoxoanion molecule and the formation of product is independent of the substitution of these cations. All of reflection peaks can be indexed to a cubic phase of ammonium POM according to JCPDS Card No. 09-0412. The diffraction peaks at 2θ values of 10.71°, 13.12°, 15.15°, 18.62°, 21.56°, 24.17°, 26.48°, 28.58°, 30.67°, 32.53°, 36.11°, 39.40°, 43.92°,47.98°, 50.68°, 51.97°, 55.68°, 57.94°, 62.62° and 64.78° are matching with the 110, 111, 200, 211, 220, 310, 222, 321, 400, 411, 332, 510, 440, 532, 541, 622, 550, 732 and 554 planes of cubic phase with the space group of Pn3m. The slight observed shifts at some 2θ values in substituted product (e.g., 24.17°, 26.48°, 36.11° and 39.40°) toward higher values can be related to the substitution of ammonium ions by X ions confirming the formation of $(NH_4)_xAg_yNi_zPMo_{12}$ compound.

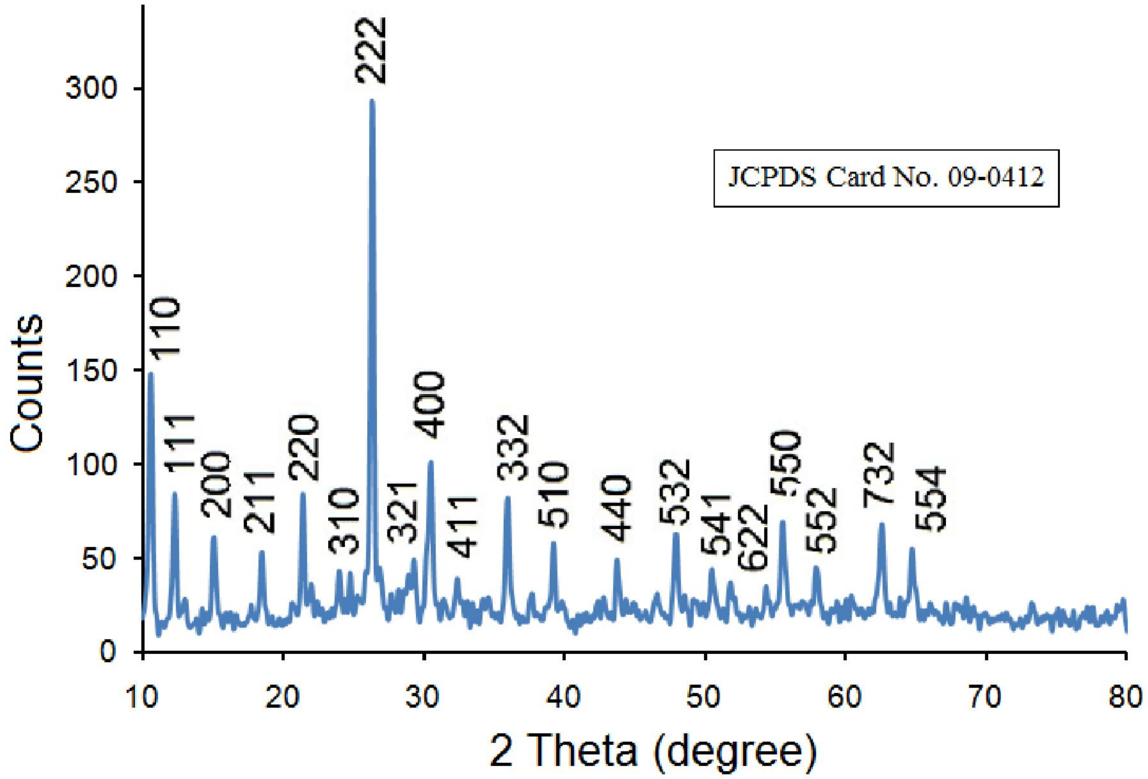

Fig. 2. XRD pattern of the resulting product.

The elemental analysis determined by EDX (shown in Fig. 3) revealed the presence of Mo, N, P, Ag and Ni elements in the prepared product. Based on the EDX and ICP results, the molecular formula of product was obtained as $(NH_4)_{1.4}Ag_{0.8}Ni_{0.4}PMo_{12}O_{40}.4H_2O$.

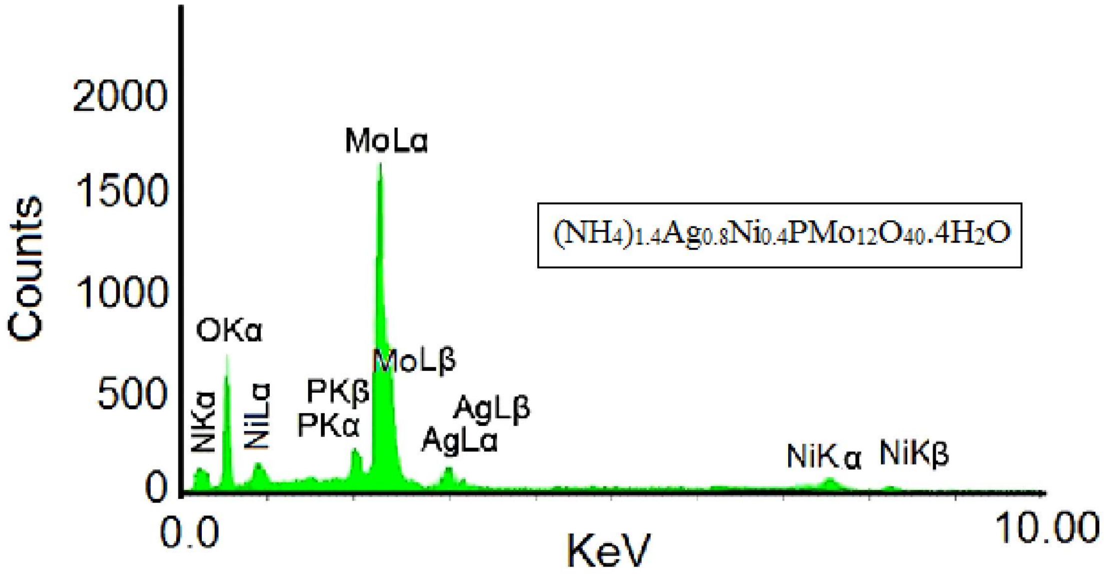

Fig. 3. EDX elemental analysis of the prepared sample ($AgNiPMo_{12}$).

Fig. 4 presents the SEM images of the prepared samples of PMo_{12} (a), and $AgNiPMo_{12}$ (b-c) using urea as the organic driving agent in the power of 360 W for 7 min. These images revealed a micro-sized spherical particulate morphology for synthesized PMo_{12} that it goes to the nano-scale with average particle size of 41 nm by incorporating the partial amounts of other counter cations to its network. It is proposed that the employed urea in addition to burning as fuel can play an important role in the arrangement of building blocks of compound due to its composition and structural nature.

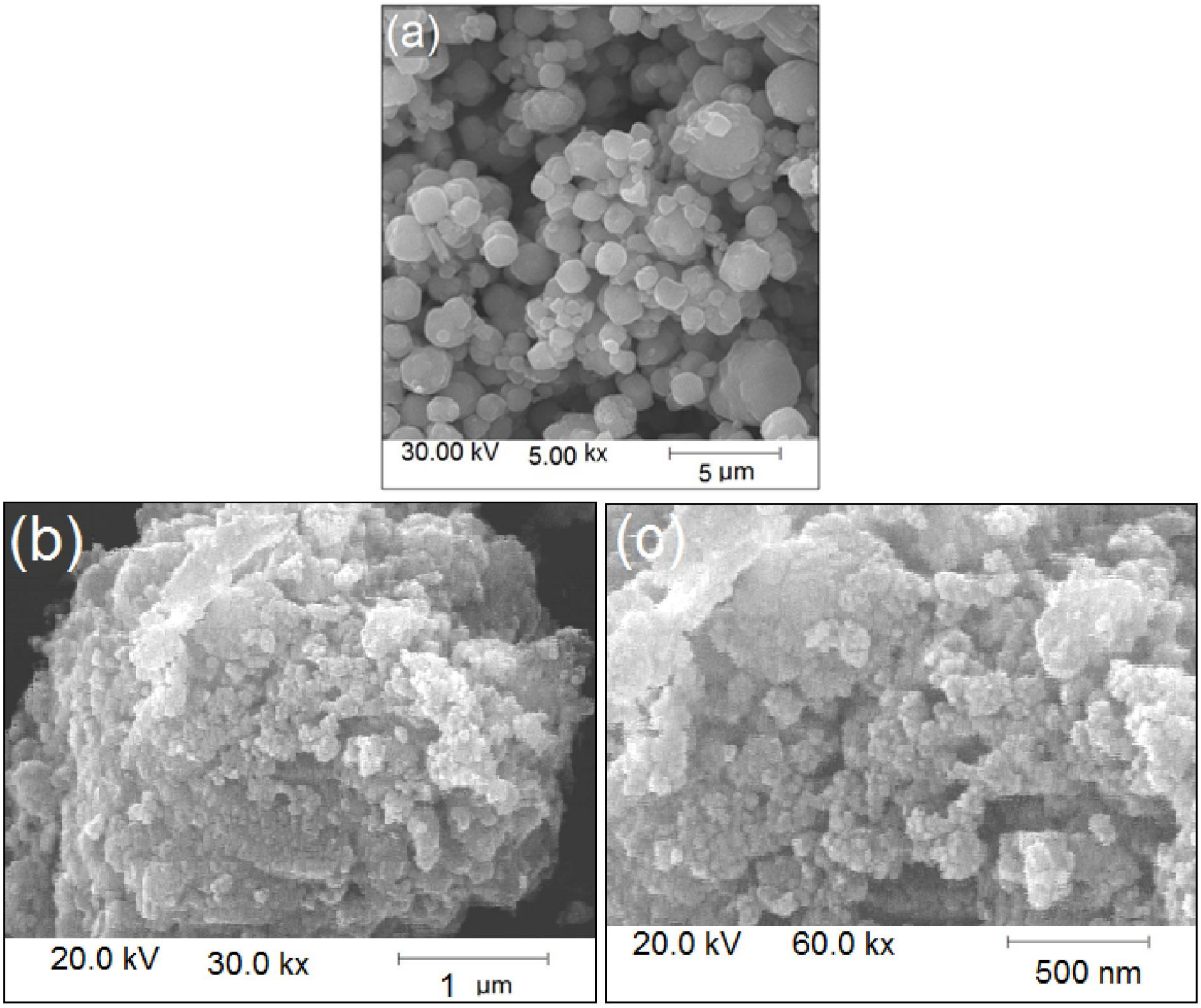

Fig. 4. SEM images of the prepared PMo$_{12}$ (a) and AgNiPMo$_{12}$ (b-c) using urea as organic driving agent in microwave heating treatment with a power of 360 W for 70 min.

Conclusions

In a summary, we successfully used a simple and rapid method for synthesis of mixed ammonium salt of PMo$_{12}$ substituted by silver and nickel counter cations using microwave heating treatment in solid phase. With the attention to the inherent nature of the employed counter ions, this group of the synthesized mixed metal oxides can be introduced as the favorable candidates for catalysis and gas sensing works. The experimental strong point of this strategy is the simplicity and rapid synthesis route in solid phase of target compound from initial materials without using complex method or materials. It can be a facile process to produce the various species of mixed polyoxoanions in nanoscale for the wide spectrum of applications.

Acknowledgements

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