

MICROWAVE-ASSISTED SYNTHESIS OF COST-EFFECTIVE AND ENVIRONMENTALLY FRIENDLY ELECTROCHEMICAL MATERIALS

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Abstract: Here we report the microwave-assisted synthesis of nanocomposites from natural zeolite and cellulose phosphate. Microwave irradiation conditions, such as irradiation power and time, required to optimize the synthesis of zeolite electrochemical materials were studied.

The growing interest in the use of zeolite-modified electrodes results from the specific framework structure, containing the three-dimensional system of cages, and channels with various shapes, sizes, and topologies (Chen, C.Y., et al). Their molecular sieve properties and ability to undergo the ion-exchange process with transition metals result in their catalytic property (Guzmán-Vargas, A., et al; Porada, R., et al). Cellulose-based materials also show interesting electrochemical properties and will be interesting to study their application of it for hydrogen production (Marzouki, R., et al).

The electrolytic model solution content of 1 M KOH and 18 g.l⁻¹ NaCl. The electrocatalysts were characterized by SEM, XRD, and BET. The electrodes are studied electrochemically by means of cyclic voltammetry, galvanostatic measurements, and Tafel slopes. The electrodes are designed and optimized in terms of the amount of composites.

Keywords: microwave assisted synthesis, cellulose phosphate, natural zeolite, seawater, electrocatalysts

INTRODUCTION

The microwave-assisted synthesis is based on the efficient heating of materials by "microwave dielectric heating" effects. This phenomenon is dependent on the ability of a specific material (solvent or reagent) to absorb microwave energy and convert it into heat. The electric component (Stass, D. V. et. al, 2000; Timmel, C. R. et al., 1996; Woodward, J. R. et. Al., 1997) of an electromagnetic field causes heating by two main mechanisms: dipolar polarization and ionic conduction. Irradiation of the sample at microwave frequencies results in the dipoles or ions aligning in the applied electric field. As the applied field oscillates, the dipole or ion field attempts to realign itself with the alternating electric field and, in the process, energy is lost in the form of heat through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself with the frequency of the applied field. If the dipole does not have enough time to realign, or reorients too quickly with the applied field, no heating occurs. The allocated frequency of 2.45 GHz used in all commercial systems lies between these two extremes and gives the molecular dipole time to align in the field, but not to follow the alternating field precisely (Baghurst, D. R. et. al., 1991; Gabriel, C., 1998). The heating characteristics of a particular material (for example, a solvent) under microwave irradiation conditions are dependent on its dielectric properties. The ability of a specific substance to convert electromagnetic energy into heat at a given frequency and temperature is determined by the so-

called loss factor $\tan \delta$. This loss factor is expressed as the quotient $\tan \delta = \epsilon''/\epsilon'$, where ϵ'' is the dielectric loss, which is indicative of the efficiency with which electromagnetic radiation is converted into heat, and ϵ' is the dielectric constant describing the ability of molecules to be polarized by the electric field. A reaction medium with a high $\tan \delta$ value is required for efficient absorption and, consequently, for rapid heating. In general, solvents can be classified as high ($\tan \delta > 0.5$), medium ($\tan \delta 0.1-0.5$), and low microwave absorbing ($\tan \delta < 0.1$).

Traditionally, organic synthesis is carried out by conductive heating with an external heat source (for example, an oil bath). This is a comparatively slow and inefficient method for transferring energy into the system, since it depends on the thermal conductivity of the various materials that must be penetrated, and results in the temperature of the reaction vessel being higher than that of the reaction mixture. In contrast, microwave irradiation produces efficient internal heating (in-core volumetric heating) by direct coupling of microwave energy with the molecules (solvents, reagents, catalysts) that are present in the reaction mixture. Since the reaction vessels employed are typically made out of (nearly) microwave-transparent materials, such as borosilicate glass, quartz, or teflon, an inverted temperature gradient results compared to conventional thermal heating (Kappe, C. O., 2004).

Microwave not only possesses instantaneous heating and hot spot effect, but also has high catalytic effect. Meanwhile, the monomer conversion is increased and the side reaction is reduced, and thus the purity and yield of obtained material are further improved (Karmakar et al., 2021).

Zeolites as natural and synthetic crystalline aluminosilicates offer many unique and specific chemical, physical, and structural properties, extremely valuable in the design of electroanalytical sensors. Zeolite modified electrodes (ZMEs) have been widely studied in the last decades, and a number of reviews concerning modification of the electrode surface with zeolites, including methods of their preparation, mechanism of charge transfer, and analytical application of ZMEs has appeared in the literature. The growing interest in the use of ZMEs in electroanalytical purpose results from the specific framework structure of zeolites containing the threedimensional system of cages and channels with various shapes, sizes, and topologies, which determine their molecular sieve properties, as well as the ability to undergo the ion-exchange process with transition metals, resulting in their catalytic property (Chen, C.Y., et al., 2012). Additionally, stability in high temperature, insolubility in most organic solvents, and resistance in acid media make zeolites an attractive modifying agent (Porada, R., et al., 2021).

Cellulose-based materials also show interesting electrical properties. For example, alkali-cellulose conductivity measurements of polyethylene oxide/carboxymethyl cel-lulose blends have revealed that for PEO/CMC with 30/70 wt.%, an electrical conduc-tivity of $5.19 \times 10^{-5} \text{ S.cm}^{-1}$ has been achieved.

EXPOSITION

Microwave-assisted synthesis of nanocomposites of zeolite/Cellulose phosphate

Microwave-assisted reactions were carried out in Microwave Reactor ROTO SYNTH Rotativ Solid Phase purchased from Milestone, Bergamo, Italy.

To obtain the protonated form of the natural zeolite, ion exchange was performed using microwave irradiation (similar to procedure describe in (Idris, A., et al., 2019). Natural zeolite (0,5 g) and 2 M ammonium chloride (NH_4Cl) (10 ml) were mixed in an open vessel. The reaction was carried out under microwave irradiation (200 W) at a hold temperature 130°C , read by IR thermometer. The reaction was completed for 15 minutes. The product was washed three times by DI water, and recovered by simple filtration and dried at 50°C under vacuum to constant weight.

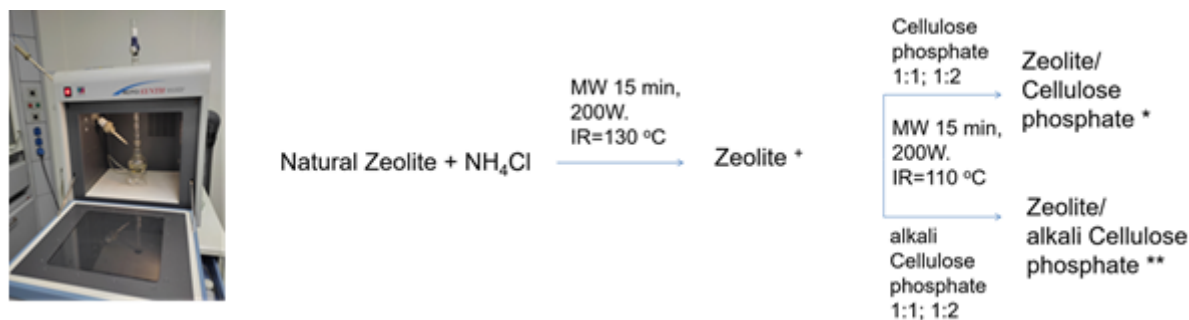


Fig. 1. Microwave-assisted synthesis of nanocomposites of zeolite and Cellulose phosphate

A novel nanocomposite of natural zeolite/Cellulose phosphate (ZCPh) was synthesized under microwave irradiation: through the addition of natural Zeolite to Cellulose phosphate or alkali Cellulose phosphate in the ratio 1:1 and 1:2 by weight, heating the reaction mixture at 200 W for 15 minutes. Reactions were performed using distilled water as a wetting agent. The preparation of the nanocomposites with the assistance of microwave irradiation, compared to conventional heating, proceeded in a shorter reaction time and in a higher yield. The reaction mixtures were washed three times by distilled water, and filtered by simple filtration and dried at 50 °C under vacuum to constant weight for all samples.

Table 1. Reaction conditions for the preparation of nanocomposites of zeolite and cellulose phosphate.

Sample	Zeolite:P-containing materials, wt	MW, watts	Reaction time, min
ZCPh-1*	1:1	200	15
ZCPh-2	1:2	200	15
ZACPh-1**	1:1	200	15
ZACPh-2	1:2	200	15

* ZCPh- Zeolite/Cellulose phosphate nanocomposite

** ZACPh- Zeolite/alkali Cellulose phosphate nanocomposite

Physico-chemical characterization of nanocomposites of natural zeolite/Cellulose phosphate

The newly synthesized composites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET).

XRD analysis

The absence of a clear diffraction peak between 19°-22.6° 2θ corresponding to the CPh, as well as and the appearance of amorphous halo are due to the reduced number of intra-molecular hydrogen bonds as a result of the introduction of phosphate groups in the structure of CPh.

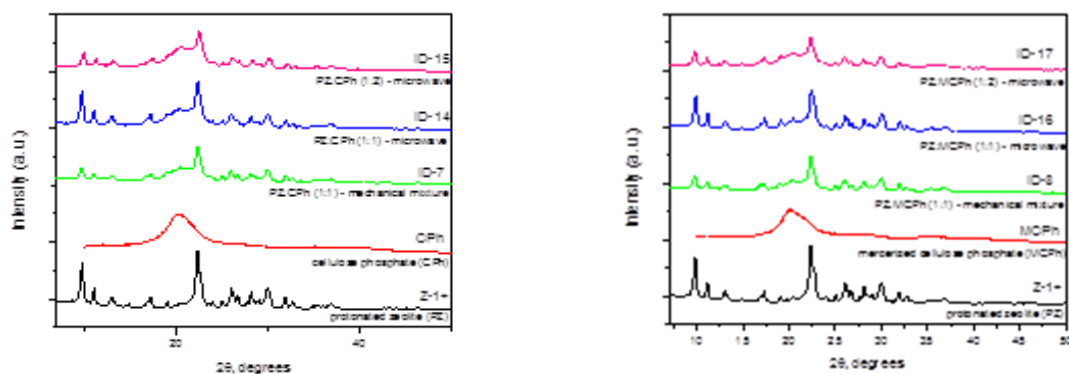


Fig. 2. XRD analysis of microwave-assisted synthesis of (a) ZCPh or (b) ZACPh nanocomposites respectively.

BET analysis

The autosorb iQ has the capability of measuring adsorbed or desorbed volumes of ni-trogen at relative pressures in the range 0.001 to slightly less than 1.0. This vol-ume-pressure data can be reduced by the autosorb iQ software into BET surface area, adsorption and/or desorption isotherms, pore size distributions, total pore volume.

On the test samples the full isotherms were measured by nitrogen physisorption and presented in the Figure 3.

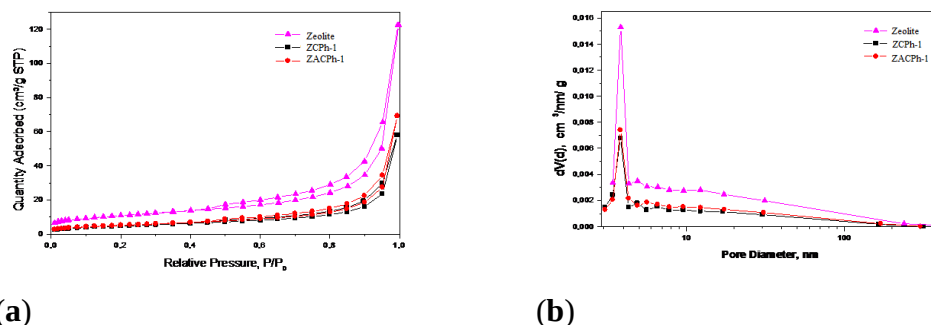
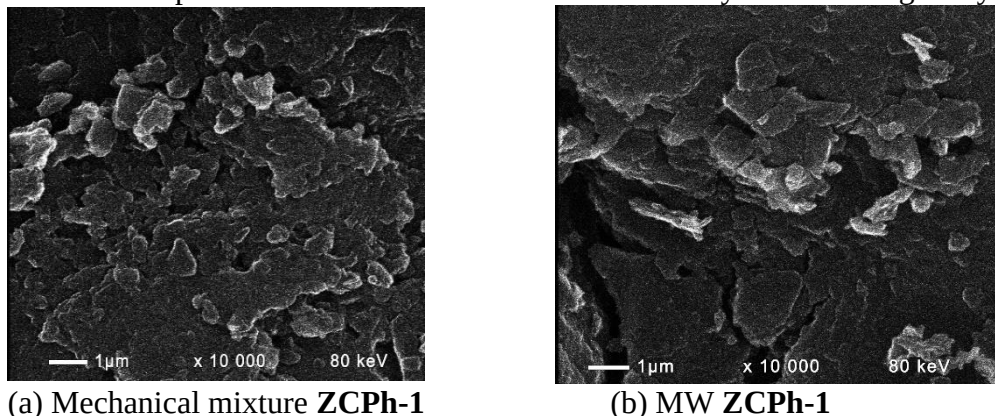


Fig. 3. BET analysis of nitrogen adsorption isotherm and pore-size distribution curves: (a) Iso-therm plots for samples of natural Zeolite, ZCPh-1 and ZACPh-1; (b) Differential curves of mesoporous size distribution for the same samples of natural Zeolite, ZCPh-1 and ZACPh-1.

SEM analysis

SEM micrographs of the samples (mechanical mixture ZCPh-1 and MW ZCPh-1) are shown in Fig. 4. It is clear that mechanical mixture ZCPh-1 shows an inhomogeneities regarding particle size distribution. After microwave-assisted synthesis of nanocomposites, a increasing the active surface area of the particle size can be observed with relatively better homogeneity (Fig. 4 (b)).



(a) Mechanical mixture **ZCPh-1**

(b) MW **ZCPh-1**

Fig. 4. SEM analysis of mechanical mixture and microwave-assisted synthesis of composite of ZCPh-1

Preliminary electrochemical study

Electrode Preparation: Different sample electrodes of the immersed type was prepared by deposition of the sample catalyst on the work surfaces of all electrodes followed by pressing and heating. The electrodes studied have geometrical areas of 1 cm². The electrodes were prepared from a mixture of the catalyst mass (constant for all electrodes – 100 mg) and teflonized carbon Vulcan XC-72 (35 % Teflon) as a binder content 50 mg/cm². The mixture was pressed onto both sides of a stainless steel current collector at 300 °C.

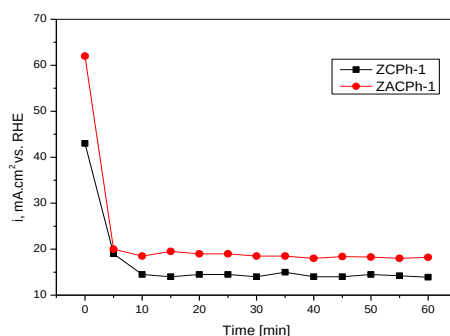


Fig. 5. Potentiosatic curve analysis of electrodes prepared from ZCPh catalysts (at MW-assisted).

Econstant = 1.4 V. Electrolyte: 1M KOH+18 g l⁻¹ NaCl, T = 20 °C.

CONCLUSION

Here we report our preliminary study on effect of microwave-assisted synthesis of nanocomposites from natural zeolite and Cellulose phosphate. Microwave irradiation conditions, such as irradiation power and time, required to optimize the synthesis of zeolite electrochemical materials were studied.

Our preliminary studies show that microwave-assisted synthesis is an appropriate method to obtaining of nanocomposites of natural zeolite and Cellulose phosphate.

Nanocomposite from natural zeolite and cellulose phosphate have very good electrochemical properties with lower overpotentials compared to the pure electrode samples tested.

This greener approach will open further research directions for the synthesis and application of cost-effective and environmentally friendly electrochemical materials.

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