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Electrochemical Study of Encapsulated Heteropolyacids in Acidic Mordenite Zeolite

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ABSTRACT

12-molybdophosphoric acid (PMo12) was encaged into HMOR zeolite by “ship in a bottle” method in aqueous phase which is strongly retained and not easily leached from the host channels. The solid was characterized by XRD prior to using it for the electrode preparation. This compound was incorporated with a carbon paste electrode for cyclic voltammetric measurements. PMo12 immobilized on the support underwent a quasi-reversible electrochemical redox reaction. In various electrolyte solutions and also changing the pH range from 0 to 5, the ΔEp remains practically constant, i.e. 179mV. The comparison of these voltammograms with those in aqueous phase shows remarkable similarities, therefore it is may concluded that this hybrid material has redox catalytic properties and high surface area, simultaneously.

Keywords: Cyclic voltammetry; Heteropolyacids; Zeolite; Encapsulation

INTRODUCTION

Since zeolite-modified electrodes are capable of combining the intrinsic properties of the crystalline aluminosilicate (mainly their ion-exchange capacity and their size selectivity at the molecular level) with electron transfer reactions, they have been largely developed during past two decades [1]. Microporous crystalline materials exhibit extremely high surface area and well defined pore size as well as high thermal stability and framework composition flexibility. In addition, the unique structural and catalytic properties of molecular sieves for structuring an electrochemical /electron transfer environment and also resistance to biodegradation have attracted considerable attention [2].

Heteropolyacids (HPAs) have a unique set of valuable catalytic properties. They consist of polynuclear molybdenum (VI), tungsten (VI), and vanadium (V) complexes, as well as many other elements as central atoms or ligands. HPAs are either oxidants or strong Brönsted acids at the same time which their use as acid catalysts is limited by a very low surface area (below 1-10 m^2/g). In order to use HPAs as solid catalysts, it is desirable to disperse them over zeolites because zeolites are suitable hosts for HPAs. The attractive properties of zeolites, such as ion exchange capacity, shape- and charge-selectivity, high thermal stability, high surface area , low cost and resistance to extreme chemical conditions, have made them

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interesting in catalysts, adsorbents, sensors and other advanced materials including zeolite-modified electrode (ZME). The redox chemistry of heteropolyacids has been studied by voltammetry of these species as solutes in aqueous solution, as components of films on electrodes in contact with a liquid phase, and as single crystals not in contact with a bulk liquid phase. Although electrochemical behavior of HPAs in water has been considerably investigated, however, less attention has been paid to the cyclic voltammetric study of HPAs supported or encapsulated in zeolites [3-8].

In this research, 12–molybdophosphoric acid (PMo12) was synthesized in some zeolites in which Ship in the bottle method was used for the process. Various techniques such as XRD, DRS and EDX-SEM have been employed to characterize these hybrid materials. The results not only show successful synthesis of PMo12 in zeolites but also confirm stability of zeolite structure during synthesis. The cyclic voltammograms of PMo12 were obtained in solution phase and impregnated in zeolites. The effect of some parameters such as pH, electrolyte and scan rate on the voltammograms was also investigated.

EXPERIMENTAL

Reagents and materials

Except as noted, all chemicals were from Merck and were used without any further purification. Aluminum sulfate was purchased from Fluka while the mordenite (HMOR) was synthesized in our laboratory based on the procedure described in the literature [9-11].Furthermore, Keggin-type PMo12 was also synthesized in the Microporous and mesoporous hosts according to the method described in literature [12].

Electrode preparation

The carbon paste electrode of this material was prepared by mixing 50 mg of HPA-zeolite, 50 mg of graphite and two drops of paraffin oil. This paste was deposited into a cavity, on the surface of a glassy carbon tip with 2 mm inner diameter . This proportion was used due to obtaining a better response in a preliminary test, however, a more detailed study about the paste composition should be made.

Electrochemical measurements were made using this carbon paste electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. All the electrochemical experiments were carried out under pure nitrogen atmosphere. The investigations of the electrochemical behavior of PMo12 incorporated into zeolite were carried out by means of cyclic voltammetry in acidic media (pH 1, apart from the pH effect experiments that the pH of solutions was adjusted with appropriate buffer).

Characterization

X-ray diffraction (XRD) measurements were performed on a Philips PW 1840 diffractometer with Cu-K_α radiation at room temperature. XRD patterns were recorded using an automatic divergence slit system.

Diffuse reflectance spectra were recorded by a UV-2100 Shimadzu spectrophotometer, equipped with an integrating sphere assembly. A special cell, loaded with the solid sample and covered by a quartz window, was used in all measurements. All the spectra were recorded at room temperature against barium sulfate and plotted in terms of absorbance. Chemical analysis of the samples was done by energy dispersive X-ray analysis (EDX) joined to a Philips XL30 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Structural stability of zeolites

The X-ray patterns of HMOR before and after post-synthesis modifications are quietly similar, which indicate the stability of zeolites structure (Fig.1). In the other hand, the Si/Al ratios for various samples are summarized in Table 1.

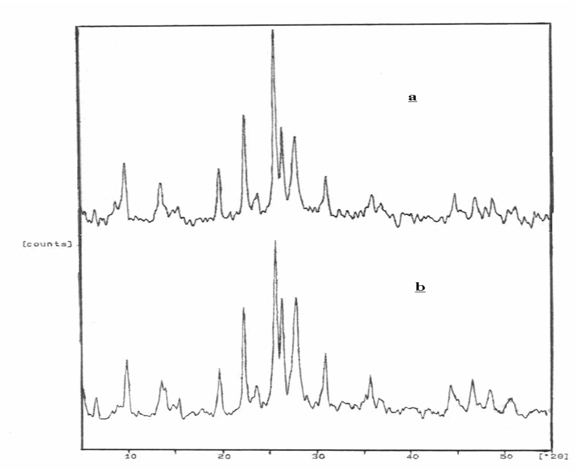

Fig.1. Powder XRD patterns of (a) NaMOR, (b) HMOR

Table1. Si/Al ratio determined by EDX-SEM

Sample	Si/Al
NaMOR	7.3
HMOR	7.4

Synthesis of PMo12 in zeolite

The diffuse reflectance spectrum of PMo12-HMOR is shown in Fig.2. This spectrum shows a wide band in the 200-500 nm regions, which is characteristic of heteropolyanions [13]. It may be ascribed to ligand to metal charge transfer.

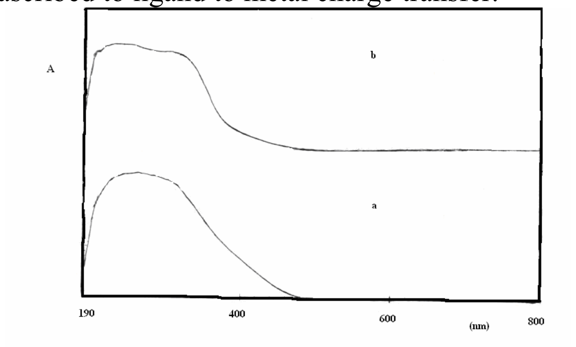

Fig.2. Diffuse reflectance spectra of (a) PMo12 (b) PMo12-HMOR.

Cyclic voltammetry

Preliminary cyclic voltammetry experiments were performed to establish the electroactivity of phosphomolybdic acid (PMo12) that is incorporated whit a host and also to compare the general redox behavior with what observed in aqueous solution. Fig.3 shows the cyclic voltammograms of PMo12-HMOR in an aqueous solution of pH 1 sodium citrate–HCl buffer at scan rate of 10mV/s. There are three pairs of redox peaks between -300 and 800 mV. Three consecutive two-electron processes whit the results reported elsewhere [14].

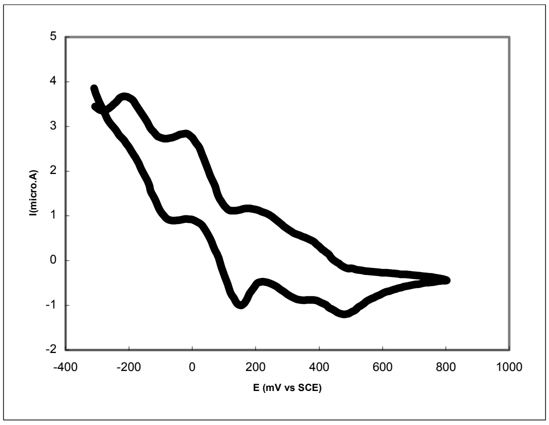

Fig.3. Cyclic voltammogram for PMo12-HMOR. Scan rate 10mV/s; sodium citrate–HCl buffer pH 1.

Since the redox potential of PMo12 in the solution phase is strongly dependent on the pH, therefore, studying of the pH influence on the electrochemical behavior of PMo12-HMOR is a very important task. The values of ΔE_p obtained for PMo12-HMOR in solution having pH between 0 and 5 remained almost constant at about 179 mV (versus SCE) (Table 2). The electrochemical behavior of ZME in various media such as phosphate buffer (pH 5.0–8.0) and sodium citrate–HCl buffer (pH 1.0–5.0) were compared by cyclic voltammetry. The excellent oxidation response was obtained in pH 1.0 sodium citrate–HCl buffer because the peak current is highest and its shape is well-defined. Therefore, 0.1 mol/L pH 1.0 sodium citrate–HCl buffer was chosen.

Table 2. Effect of solution pH on the E_{pc} and E_{pa} [a]

pH	E_{pc} (mV vs SCE)	E_{pa} (mV vs SCE)	ΔE_p (mV vs SCE)
0	-28	152	180
1	-29	154	183
2	-27	151	178
3	-29	150	179
4	-28	150	178
5	-27	153	180

[a] For the second pairs of redox peaks

Cyclic voltammograms obtained at different scan rates that ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) increases at higher rates. This is an indication that the kinetic of electron transfer on the electrode surface is not sufficiently fast due to the matrix nature with considerable internal resistance.

Fig.4 shows influence of scan rates at the PMo12-HMOR in pH= 1 on the response current. When the scan rates are in 10–220 mVs^{-1}, the cathodic peak currents are directly proportional to the square root of scan rates, indicating that electrode process is controlled by diffusion.

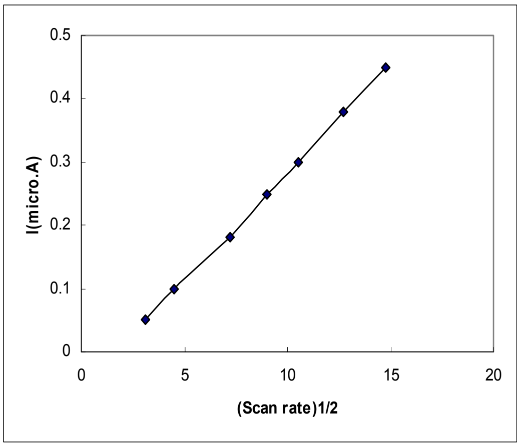

Fig.4. Variation of I_p with the square root of the scan rate for the PMo12-HMOR in pH 1 sodium citrate–HCl solution.

CONCLUSION

PMo12 is strongly adsorbed by acidic mordenite zeolite (HMOR) and it is not leached from the matrix even in concentrated electrolyte solution. The redox potential of the incorporated PMo12 is not influenced by the electrolyte solution pH range of 0 to 5. The comparison of the voltammograms in solution phase and into the zeolite shows remarkable similarities between them and therefore, it is may concluded that this hybrid material preserves its redox catalytic properties together with high surface area, simultaneously.

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