

Proton conducting composites of heteropolyacids loaded onto MCM-41

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Abstract

Proton conducting composites have been prepared by loading heteropolyacids, namely tungstophosphoric (TPA) acid and molybdophosphoric (MPA) acid, into MCM-41 molecular sieve. The synthesis procedure was optimized to ensure maximum loading of TPA and MPA with negligible leaching of solid acids. The proton conductivity of the composite powdered materials was found to depend on the loading of the heteropolyacids and strongly affected by the presence of water in the solid. The highest proton conductivity of the order of 10^{-2} S cm⁻¹ at room temperature was found for the TPA loaded MCM-41. The prepared materials have been characterized by FTIR, SEM and X-ray diffraction, which confirm the presence of heteropolyacids into MCM-41 molecular sieve structure. Leaching study carried out on the composite solids confirmed that the material leached out through the composite solids was negligible and hence almost complete loading of heteropolyacids into the MCM-41 structures was ensured. The new material combines the high thermal and structural stability of MCM-41 with outstanding conductivity of heteropolyacids. The high conductivity and negligible leaching of this material makes it suitable for use in the preparation of membranes for use in fuel cells and other electrochemical devices.

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1. Introduction

Mobil catalytic materials of number 41 (MCM-41) belong to the family of mesoporous molecular sieves discovered in the 1990s [1]. Due to its peculiar characteristics, large internal surface area and favorable uniformity but easily controlled size of the pore, the ordered mesoporous molecular sieve MCM-41 has attracted considerable interest in physics, chemistry, materials science and other relevant areas [2]. This novel mesoporous solid have been suggested to use as shape/size selective adsorbents, hosts for quantum structures, catalysts, catalyst supports and proton conductors [2,3]. This family of materials has large channels in a hexagonal array, long range order and surface areas above 900 m² g⁻¹ [4]. These striking features together with their exceptional

adsorption properties make them promising candidates for incorporation of proton conductors for fuel cell applications.

Recently, solid proton conducting materials have become of greater interest due to their potential in various electrochemical devices, such as fuel cells and batteries [5]. Although, a vast number of various solid electrolytes have already been identified, but the development of chemically and thermally stable superionic conductors still remains one of the prime goals of research in solid state electrochemistry and material science [5]. There have been some studies reported in the literature for the development of solid proton conducting materials based on the modification of mesoporous structure of silica and zeolites [3–8]. These include mesoporous zirconium and titanium phosphates, composites of heteropolyacid hydrates dispersed with insulating Al₂O₃, phosphotungstic acid–tin mordenite composites, sulfonic acid functionalized mesostructured porous silica. In all of these studies, the leaching aspect of the composite solids

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when exposed to water has not been discussed, which is a major issue in these composite materials. Their chemical and long term stability in the humidified fuel cell environment is not known. Moreover, some of these materials do not show very high conductivity, high enough to be considered for use in fuel cell applications. In the present study, novel solid proton conductors with the help of MCM-41 and heteropolyacids (TPA and MPA) have been synthesized and characterized. The new composite material would combine the high thermal and structural stability of MCM-41 with outstanding conductivity of heteropolyacids, which makes it suitable for use in fuel cells and other electrochemical devices, but without disadvantage of mobile heteropolyacids (HPAs).

Heteropolyacids have been well known for their exceptionally high proton conductivity [7] and are one of the potential inorganic modifiers as they have demonstrated high conductivity. HPAs are known to have different hydrated structures depending on the environment. In the dehydrated phase, in polar solvents, the primary structure is called a Keggin unit. The Keggin unit consists of a central atom in a tetrahedral arrangement of oxygen atoms surrounded by 12 oxygen octahedra connected with tungsten or molybdenum. There are four types of oxygen atoms found in the Keggin unit: the central oxygen atoms, two types of bridging oxygen atoms and the terminal oxygen atoms. In the hydrated phase, water moieties bridge the HPA molecules by forming hydronium ions, such as $H_5O_2^+$. The proton conduction mechanism for the heteropolyacids has been extensively investigated [7].

Earlier efforts for using pure HPAs as a solid electrolyte suffers from some drawbacks due to their high solubility in water and alcohols. It would be interesting to investigate the proton conductivity of the HPA incorporated MCM-41 system [9,10]. It is suggested that specific interactions between HPAs and MCM-41 could have a significant influence on fuel cell performance at elevated temperatures. Since MCM-41 is a mesoporous material, it is expected that dispersion of HPAs into its pores will be uniform and contribute to high proton conductivity due to the presence of strong acid sites. Though methanol permeation studied has not been carried out in this study, but it is expected that due to the pore occupation of MCM-41 by HPAs will also reduce methanol permeation which is considered to be one of the bottlenecks of DMFCs.

This paper describes the preparation and characterization of tungstophosphoric acid (TPA) and molybdophosphoric acid (MPA)/MCM-41 molecular sieve solid powders with various weight percentages of HPAs into mesoporous MCM-41 structure. Proton conductivity was measured with the help of impedance analyzer at ambient as well as fully hydrated conditions. Leaching study was carried out on the prepared materials in order to ensure that heteropolyacids are not leached out from MCM-41 structure. The leaching study confirmed that HPAs are completely incorporated into MCM-41. The new composite material combines the high thermal and structural stability of MCM-41 with outstanding conductivity of heteropolyacids.

2. Experimental

2.1. Preparation of heteropolyacids loaded MCM-41

Analytical grade 99.5% tungstophosphoric acid and molybdophosphoric acid were used as received from Fluka chemicals. The MCM-41 was synthesized according to the procedure of Ref. [11] and details are described therein. The MCM-41 used here has a surface area of $883 \text{ m}^2 \text{ g}^{-1}$, pore volume of 0.99 cc g^{-1} and had average pore size of 22.5 \AA .

In order to establish the procedure by which strong HPA and MCM-41 molecular sieve interaction would be achieved, three procedures were adopted to impregnate HPAs on MCM-41 molecular sieve. A predetermined amount of TPA was dissolved in distilled water and few drops of dilute HCl were added in order to avoid hydrolysis of TPA. Then required amount of MCM-41 was added to make a suspension. The suspension was stirred and evaporated at 80°C until dryness. Then the solid was ground to fine particles and dried at 200°C for 6 h in air flowing oven.

The second procedure involved overnight soaking of the suspension at room temperature before evaporating at 80°C following the same procedure mentioned above. In the third instance, the suspension was homogenized using ultrasonic gun in pulsating mode of operation for 30 min. After that, the suspension was stirred and evaporated at 80°C until dryness following further drying at 200°C as mentioned in the first procedure. The solids were then finely ground and collected for further characterization.

The resulting materials were evaluated by washing the HPA supported MCM-41 molecular sieve with hot water at 80°C in a beaker for 1 h and then analyzing the washing by atomic absorption spectroscopy for tungsten. The results of AAS analysis showed minimum amount of the TPA was leached out in the case of samples prepared by ultrasonic treatment. This procedure was followed to prepare other samples with different loadings and also using MPA supported MCM-41 molecular sieve.

2.2. Leaching study on prepared materials

To check the leaching of the loaded solid acids from the prepared samples to ensure negligible HPA extraction from MCM-41, a leaching study was carried out in a flow apparatus. The flow apparatus consists of a simple U-tube, one end of the U-tube was connected to distilled water supply, while the other end was connected to the conical flask to collect the distilled water passed through the solid powder in the midst of U-tube. Powdered solid powder was put at the bottom of the tube and both the ends of the tube were packed with glass wool. The U-tube was then immersed into a beaker with an oil bath, which was heated and maintained at 80°C throughout the experiment. The water passed through the solid powder was thus collected and analyzed for molybdenum and tungsten metals, respectively, with the help of atomic absorption spectrophotometer (AAS) and inductively coupled plasma

(ICP) techniques. The water used here was distilled twice in order to ensure purity.

2.3. Proton conductivity measurements

The impedance spectroscopy technique was used to carry out the proton conductivity measurements of the synthesized powders. The impedance measurements were performed over the frequency range 0.1×10^6 to 1.2×10^6 Hz with oscillating voltage 10 mV, using a PC controlled SI 5210 impedance/gain-phase analyzer. The impedance data were corrected for contribution from the empty and short-circuited cell. Proton conductivities for MCM-41, tungstophosphoric acid, molybdophosphoric acid and composite powders from MCM-41 with different weight percentage loadings of TPA and MPA were measured. Proton conductivity mechanism in solids is strongly a water assisted phenomenon which is extremely dependent on the water present. The detailed procedure of conductivity measurements used in this work is described elsewhere [12].

Measured amounts of dry solids and water were mixed and the wet powder was immediately placed into a 2 mm inner diameter Teflon spacer which was then placed in between the two stainless steel electrodes of the conductivity cell and clamped therein. Since the design of conductivity cell is such that four clampers are equidistant which ensure homoge-

neous and equal pressure in all of the cases. Moreover, equal amounts of each prepared powder samples were also taken for conductivity measurement. Also, the use of Teflon spacer ensured almost zero conductivity because of the insulation properties of Teflon material between the electrodes. The sample weight was measured before and after the impedance test in order to detect any loss of water during the duration of measurement. Since the duration of acquisition of a complex impedance spectrum did not exceed more than 10 min, the hydration degree did not change by more than 10–20%. The proton conductivity values from these impedance measurements were calculated as a function of solid/water weight ratio.

The advantage of above-mentioned measurement method apart from its quickness is that it allows the study of solid behavior at water content higher than at 100% RH. This sounds important because some applications of solid electrolytes involve the direct exposure of materials with liquid water such as in the case of direct methanol fuel cell applications.

2.4. Characterizations of the solids

2.4.1. FTIR spectra

FTIR spectra were measured in transmittance mode on a Perkin-Elmer FC-16 FTIR spectrometer. Spectra were taken

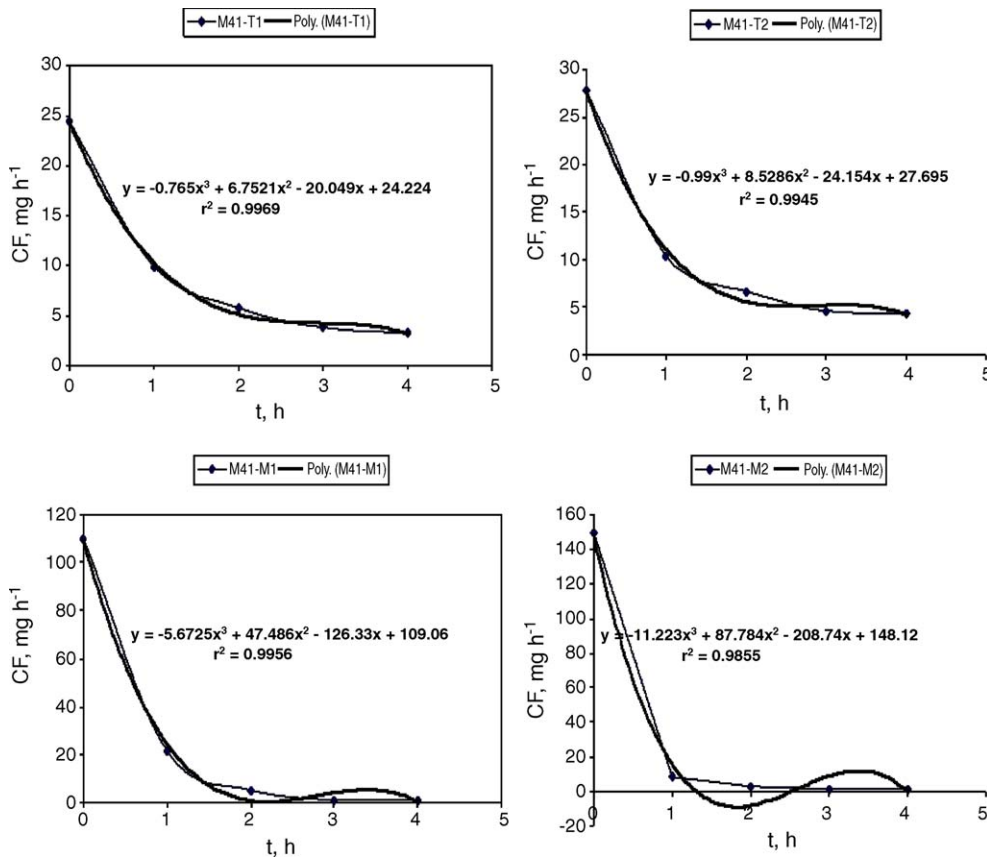


Fig. 1. Leaching plots of MCM-41 loaded with heteropolyacids (TPA and MPA).

by making pellet of different powder samples with potassium bromide (KBr). Around 4–5 mg of sample was mixed with approximately 200 mg of KBr to prepare the pellets. The spectrum for each pellet was taken with the above-mentioned spectrometer in the range 400–4000 cm^{-1} .

2.4.2. XRD patterns

X-ray powder diffraction measurements were carried out on a JEOL JDX-3530 X-ray diffractometer instrument. Each sample was gently ground in an agar pestle and mortar. The fine powder was packed into a sample holder having a diameter of ~ 25 mm and depth of ~ 3 mm. The surface of the packed sample was smoothed with a piece of flat glass. Cu broad focus tube at 40 kV and 40 mA was used with a divergence slit of 1° and scatter slit of 1° . A curved graphic monochromator was used with a receiving slit of 0.2 mm scanning speed and interval of data collection was 0.01° and 2θ (s^{-1}), respectively. The diffraction patterns were recorded over a 2θ range of 4– 80° .

2.4.3. Scanning electron micrographs (SEM)

For SEM images of solid powders, small amounts of the samples were spread on adhesive conductive copper tapes attached to a sample holder and examined with the JEOL (Model 5800LV SEM) scanning electron microscope with low vacuum capability. All of the images were taken in backscattered electron (BEI) mode.

3. Results and discussion

3.1. Leaching study of prepared powders

The specifications and description of the samples used in this work are given in Table 1. Results of leaching study showed strong interaction of heteropolyacids with MCM-41. Table 2 shows the amounts of tungsten and molybdenum detected through inductively coupled plasma analysis and atomic absorption spectrophotometer techniques. It is clear from Table 2 that the amount leached out through the powdered material in flow studies is quite negligible as compared to loaded amounts of heteropolyacids onto MCM-41. This study confirmed that the material leached out through the experiment was negligible and hence almost complete load-

Table 1

Abbreviations used for various powder samples used in the work

Powder samples	Sample description
M41	Pure MCM-41
T	Tungstophosphoric acid (TPA)
M	Molybdophosphoric acid (MPA)
M41-T1	MCM-41 + 40% TPA
M41-T2	MCM-41 + 50% TPA
M41-M1	MCM-41 + 40% MPA
M41-M2	MCM-41 + 50% MPA

ing of HPAs into the MCM-41 molecular sieve structures was ensured. The results indicate that TPA is relatively strongly bound to the MCM-41 as compared with that of MPA. However, overall leaching of the metals in both the cases is very small comparing the amount of HPAs loaded, i.e. 40 and 50%. Results reported in Table 2 are also plotted in Fig. 1 as CF versus time t , where CF is the mass flow rates of heteropolyacids in mg h^{-1} . From these plots, the total amounts of HPAs leached out have been calculated. The plots obtained between CF and time t (in hours) has been fit using 3rd order polynomial. These 3rd order polynomials in all cases have been integrated between the limits 0 h (i.e. at the start) and 4 h to obtain the total amounts of leached heteropolyacids. In case of TPA loaded MCM-41, it was found out that 3.2% of the initial amount of TPA was leached out in case of solid powder containing 40 wt.% TPA, while 3.5% of the initial amount of TPA was leached out of solid powder containing 50 wt.% TPA. That means 36.8 and 46.5 wt.% of TPA was still present on MCM-41 in case of 40 and 50 wt.% initial loading of TPA on MCM-41, respectively. In case of MPA loaded MCM-41, it was found out that 7.2% of the initial amount of MPA was leached out in case of solid powder containing 40 wt.% MPA, while 7% of the initial amount of MPA was leached out of solid powder containing 50 wt.% MPA. That means 32.8 and 43 wt.% of MPA was still present on MCM-41 in case of 40 and 50 wt.% initial loading of MPA on MCM-41, respectively. It is also clear from Fig. 1 that the leached amounts reduced to few ppm after first 4 h of continuous flow through the composite solid powders and afterwards were negligible. This sounds interesting because some applications of solid electrolytes involve the direct exposure of materials with liquid water for long periods of time, such as in the case of direct methanol fuel cell applications. So, membranes pre-

Table 2

Results of leaching study for composites of TPA and MPA loaded MCM-41

Number of hours	M41-T1			M41-T2			M41-M1			M41-M2		
	C (mg l^{-1})	F ($1/\text{h}^{-1}$)	CF (mg h^{-1})	C (mg l^{-1})	F ($1/\text{h}^{-1}$)	CF (mg h^{-1})	C (mg l^{-1})	F ($1/\text{h}^{-1}$)	CF (mg h^{-1})	C (mg l^{-1})	F ($1/\text{h}^{-1}$)	CF (mg h^{-1})
0	81.5	0.3	24.45	92.9	0.3	27.87	366	0.3	109.8	500	0.3	150
1	32.7	0.3	9.81	34.6	0.3	10.38	72	0.3	21.6	28	0.3	8.4
2	19.4	0.3	5.82	22.1	0.3	6.63	18	0.3	5.4	11	0.3	3.3
3	12.8	0.3	3.84	15.2	0.3	4.56	4.5	0.3	1.35	4.7	0.3	1.41
4	11.1	0.3	3.33	14.5	0.3	4.35	4.1	0.3	1.23	4.5	0.3	1.35

C is the concentration in mg l^{-1} , F the flow rate of water through the U-tube and CF is the mass flow rate of the HPA at different time intervals.

Table 3
Conductivity of composite powder samples measured at ambient conditions

Powder sample no.	Conductivity (mS cm^{-1})
M41	0.011
T	3.37
M	0.084
M41-T1	0.023
M41-T2	0.033
M41-M1	0.019
M41-M2	0.031

pared from this material would be stable as solid HPAs will not come out of the polymer matrix and hence is promising for use in methanol fed fuel cell.

3.2. Proton conductivity

The results of proton conductivities of powder samples at room temperature for all of the above-described materials are given in Table 3. The results shown in Table 3 indicate that as weight percentage loading of heteropolyacids increases in MCM-41, proton conductivity also increases. For example, MCM-41 molecular sieve with 40 and 50 wt.% of TPA exhibit conductivities at 25 °C of 0.023 and 0.033 mS cm^{-1} , respectively, while MCM-41 containing 40 and 50 wt.% MPA exhibit conductivities at 25 °C of 0.019 and 0.031 mS cm^{-1} , respectively. For pure MCM-41, the proton conductivity at room temperature (25 °C) was found to be 0.011 mS cm^{-1} , which is enhanced considerably to high values by loading of heteropolyacids into the MCM-41 structure. Hence, incorporation of HPAs onto MCM-41 increased its conductivity to high values, which confirmed that HPAs are present in the MCM-41.

Results of proton conductivity at various water contents of MCM-41 loaded HPAs with 40 and 50 wt.% of TPA and

MPA, respectively, are plotted in Figs. 2 and 3. It can be seen from these figures that conductivity of these composite powders is very sensitive to water adsorption and increases with the variation of water contents by two to three orders of magnitude. It changes for instance from $1.98 \times 10^{-2} \text{ mS cm}^{-1}$ for dry MCM-41/TPA to 10.6 mS cm^{-1} for 50 wt.% water content. Also, it was observed for all solid powders that conductivity increase is marginal at low water content up to 20% but above 30%, it jumps to very high values to more than 10–15 times than at 30 wt.% water content.

As is known, the proton conduction in general is a water assisted phenomenon and water has a profound effect on proton conductivity. Though proton conductive membranes in general have some inherent water which helps in maintaining a certain level of proton conductivity but the presence of extra water during a particular application, e.g. electrochemical application enhances the proton conductivity many times. Higher water uptakes generate a more solvated species, which is needed for high proton conductivity. In all cases, proton transfer is obviously associated with acid sites grafted within the pores. Hydration allows bridging acidic sites assisting ion hopping and providing additional charge carriers [6]. The heat of hydration for solid proton conducting hydrates (which can be taken as measure for the hydrogen bond interaction) strongly decreases with increasing hydration whereas the water-diffusion coefficient increases with progressive hydration. Therefore, protonic conductivity increases with increasing water content for all solid proton conducting hydrates [13]. The samples of TPA/MCM-41 display higher conductivity than MPA/MCM-41 samples as TPA is the strongest HPA in the Keggin series and possessed highest conductivity. In pure MCM-41 sample, there are no acid functions as those of HPAs, so its conductivity did not change appreciably with increase in water content. However, a large number

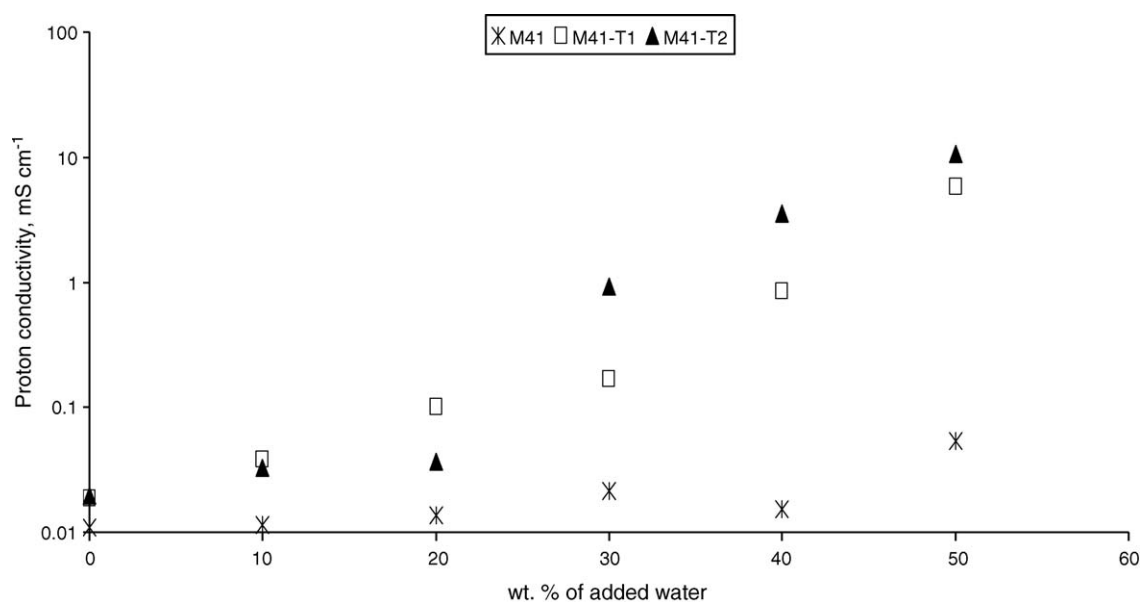


Fig. 2. Proton conductivity as a function of water content (wt.%).

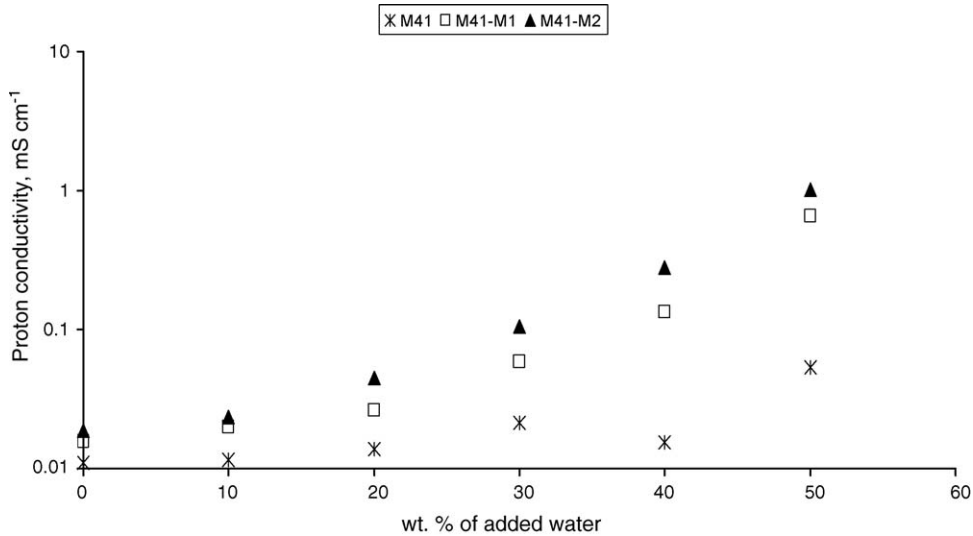


Fig. 3. Proton conductivity as a function of water content (wt.%).

of silanol groups present in the MCM-41 structure may be desirable for designing excellent proton conductor.

3.3. FTIR spectra

The infrared spectra of pure tungstophosphoric acid powder and TPA/MCM-41 composite powder are displayed in Fig. 4. IR spectra of the pure molybdophosphoric acid powder and its composite MPA/MCM-41 are given in Fig. 5. For pure TPA, six characteristic peaks of its Keggin structure were observed at 1078, 980, 888, 788, 590 and 524 cm^{-1} , respectively [14], while MCM-41 shows strong IR bands

in the range 750–1250 cm^{-1} . To confirm the presence of heteropolyacids into MCM-41 framework, IR spectra of composite powders with 40 and 50% TPA are also shown in Fig. 4. It can be observed that the characteristics peaks of tungstophosphoric acid dominate over the peaks of MCM-41 which shows the presence of characteristic Keggin anion even in the synthesized solid powders [15]. Pure tungstophosphoric acid shows distinctive, strong IR bands in the range of 500–1200 cm^{-1} , while pure MCM-41 shows a weak shoulder at about 960 cm^{-1} which broadens to 964 cm^{-1} in case of 40 wt.% loading of TPA and 982 cm^{-1} in case of 50 wt.% loading. This band-broadening can be attributed

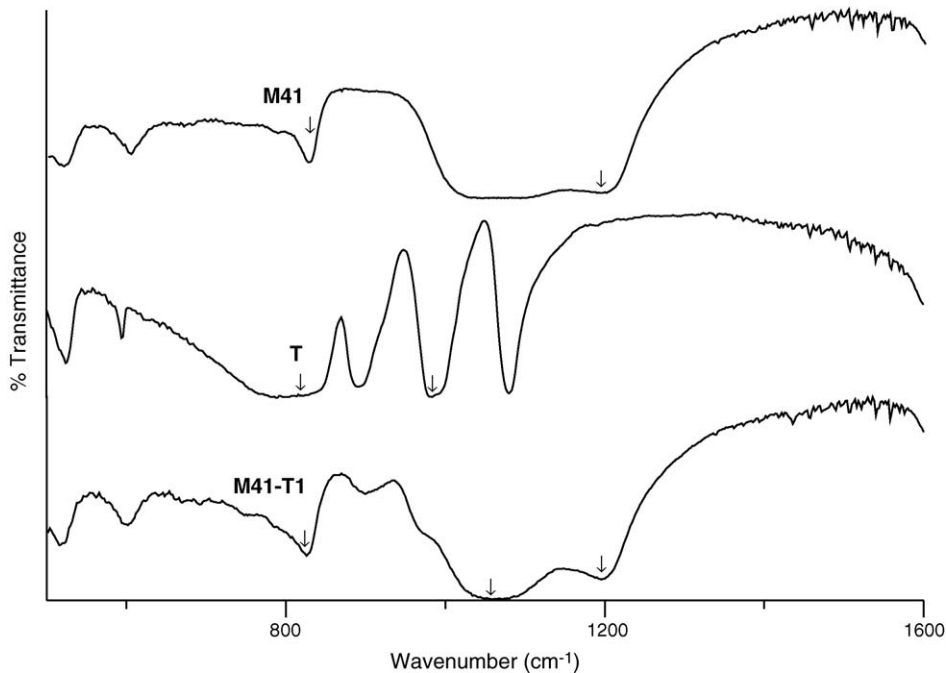


Fig. 4. FTIR spectra for M41, T and M41-T1.

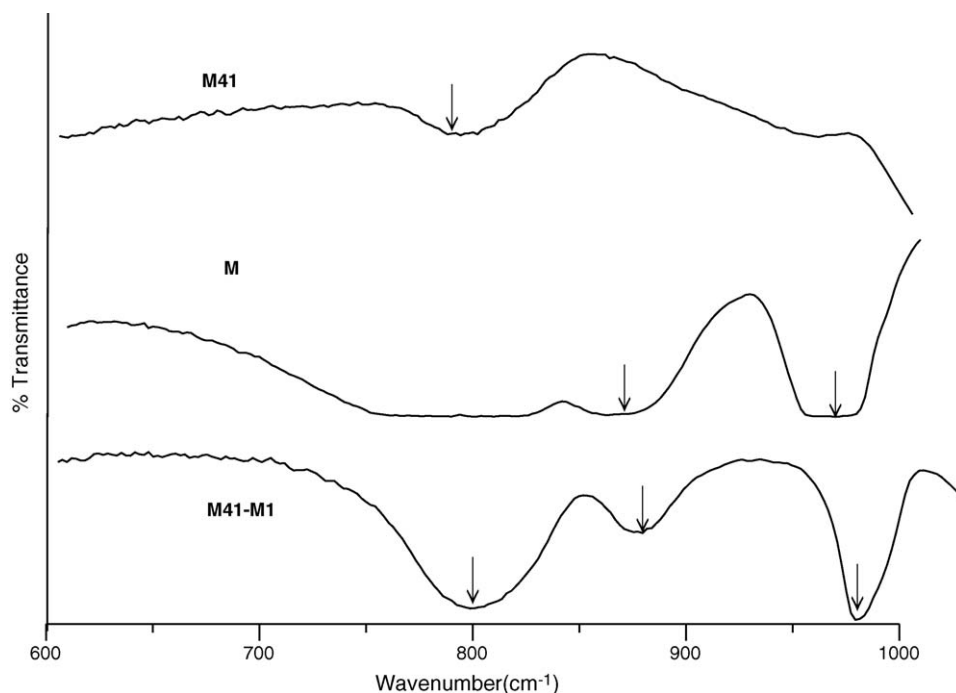


Fig. 5. FTIR spectra for M41, M and M41-M1.

to heteropoly anion which dominates over the characteristic peaks of MCM-41 [16] and is probably due to the chemical interaction between HPA anion and the MCM-41 inner sphere. These results also support the observation from the impedance spectroscopy for the proton conductivity measurements. Since MCM-41 is barely proton conductive, but as the loading of heteropolyacids into MCM-41 increased, its proton conductivity becomes very high for 40 and 50 wt.% loading. A similar behavior was observed for solid composite powders of molybdophosphoric acid loaded into MCM-41, whose FTIR spectra are shown in Fig. 5.

3.4. X-ray diffraction patterns

X-ray diffraction is a strong tool to measure the crystallinity of the materials and hence their symmetry and regularity. X-ray diffraction patterns of pure MCM-41, pure TPA and MCM-41 with 50 wt.% tungstophosphoric acid are shown in Fig. 6. From the figure, it is evident that pure MCM-41 is almost amorphous [14], while pure TPA is highly crystalline. However, the diffraction pattern of MCM-41 with 50 wt.% TPA is not amorphous and shows crystallinity with less intense peaks as compared to pure TPA. Since MCM-41 powder is not crystalline at the atomic level, so no reflections at higher angles are observed. Actually, the patterns obtained for MCM-41 represents poor crystallinity of the material and indicates a distortion of the long range ordering of the mesoporous structure and/or badly built hexagonal arrays. This is perhaps the result of the incorporation of aluminum into the silicate walls, causing structural irregularity. On the other hand, XRD patterns of MCM-41 with 50 wt.%

of TPA shows strong and regular peaks in the range of 4–40°. The strongest peaks for TPA occur at about 6.8° with other significant peaks at 8.4°, 10.8°, 13.5°, 15.96°, 17°, 18.2°, 20.2°, 22°, 25°, 26.4°, 27.9°, 29° and 35.64°, respectively. However, the XRD pattern of MCM-41 with 50 wt.% TPA shows its strongest peak at about 7.8° which is shifted from 6.8° in case of pure TPA. This shift could be due to the specific interactions of MCM-41 with TPA and perhaps also due to the heteropoly anion dominance over the characteristics

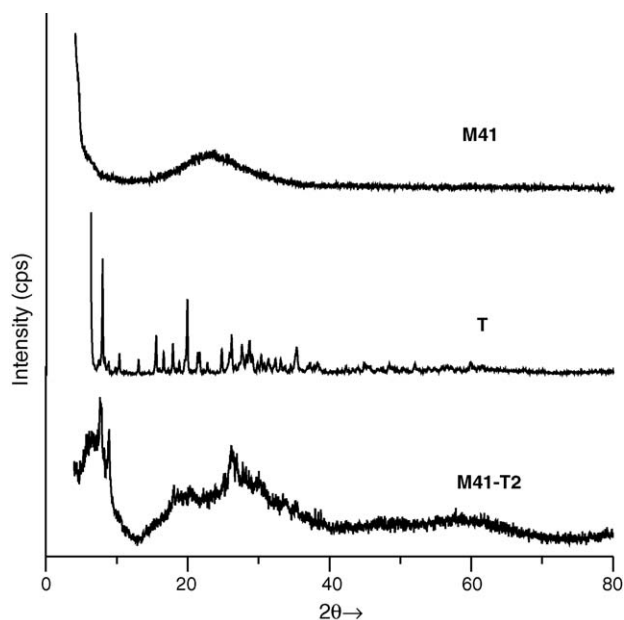


Fig. 6. XRD spectra for M41, T and M41-T2.

peaks of MCM-41. These specific interactions may be due to the corner-shared oxygen (O_c) present in the heteropoly anion, nevertheless, interaction due to edge-shared (O_e) oxygen atoms cannot be ruled out completely.

Similarly, it is clear from the XRD pattern of pure molybdophosphoric acid given in Fig. 7 that it shows excellent crystallinity and regularity with a large band of intense peaks between 4° and 60° . The strongest peaks occur at about 26.2° with other significant peaks occurring at 10.6° , 15° , 21.4° , 30.5° , 36° , 39.2° , 43.8° , 47.96° and 55.6° , respectively. The little shift in the most intense peak from 26.2 to 26.4 was observed in MPA which could be considered negligible. This observation shows that the characteristics peaks of MCM-41 do not affect the characteristics Keggin structure of MPA and thus confirmed the conclusions drawn from impedance spectroscopy measurement which showed considerable high protonic conductivities for MPA loaded MCM-41, especially for 50 wt.% of MPA loaded into MCM-41. Apart from the most intense peak, other significant peaks of MPA also do not get affected in presence of MCM-41 and hence confirm that the solid composite material with 50 wt.% of molybdophos-

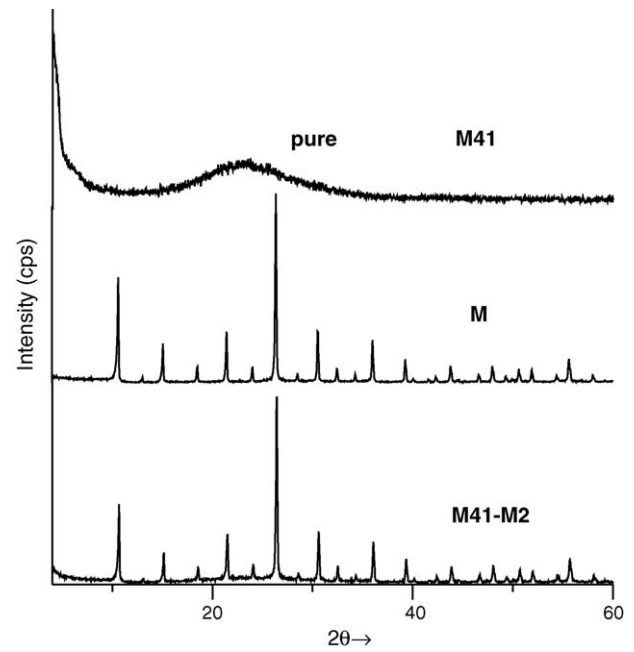


Fig. 7. XRD spectra for pure M41, M and M41-M2.

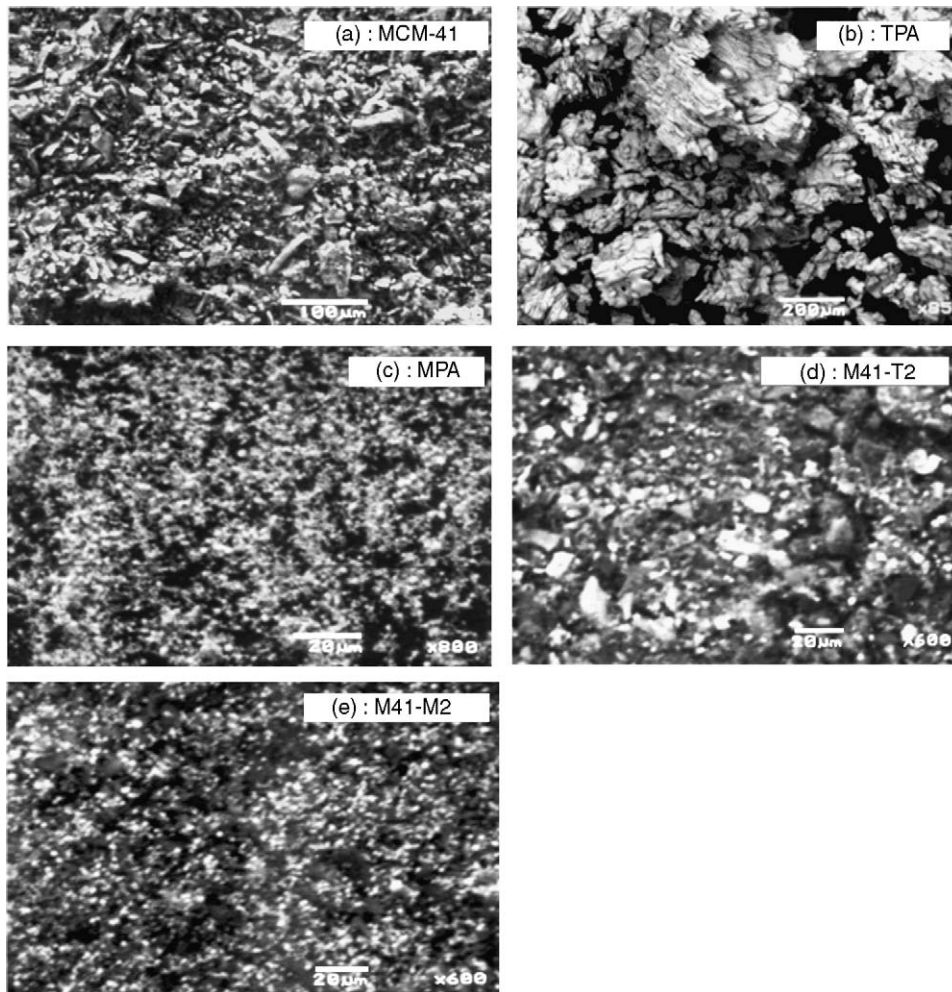


Fig. 8. SEM images of: (a) pure MCM-41; (b) TPA; (c) MPA; (d) M41-T2; (e) M41-M2.

phoric acid is highly proton conductive with no significant change in crystal structure. Therefore, XRD results indicate that HPAs are finely dispersed on the MCM-41 surface.

3.5. SEM images

SEM images of pure MCM-41, tungstophosphoric acid, molybdophosphoric acid and composite material of MCM-41 with 50 wt.% of each TPA and MPA are shown in Fig. 8. SEM image of pure MCM-41 (Fig. 8a) shows almost regular dispersion of silica and alumina channels which consequently evidences the large pore sizes in the crystal structure, while tungstophosphoric acid shows (Fig. 8b) mixture of small crystals with few big crystals [17,18]. These big crystals could be possibly due to large polyoxometalate anion present in TPA which is primarily responsible for its regular crystal structure and high proton conductivity. Molybdophosphoric acid shows a uniform crystal structure as compared to TPA; however, the presence of heteropoly anion also found (Fig. 8). The presence of Keggin structure is not so prominent in MPA as compared to TPA because molybdenum (Mo) atom is far less in size compared to tungsten (W).

Observation of SEM images of MCM-41 with 50% of TPA accords with the SEM image of pure MCM-41, which can be explained that TPA is well dispersed into MCM-41 (Fig. 8d). Although some big cluster-like areas are also seen but they may be due to heteropoly anions present in TPA. As described earlier, the protonic conductivities of solid powders with 50 wt.% TPA was found to be considerably high, which could be due to these heteropoly anions present inside the pores (probably) as well as on the surface of MCM-41. On the other hand, the SEM image of MCM-41 with 50 wt.% of molybdophosphoric acid (Fig. 8e) shows absolute uniformity with regular crystal structure arrays as that of pure MPA. This could again be due to the compatibility of MPA and MCM-41 material as compared to TPA and MCM-41, however, high proton conductivity factor in case of TPA dominates over MPA and that is why we got higher conductivities in case of TPA loading rather than MPA loading. So, it can be concluded from these loaded heteropolyacids in MCM-41 that from structural point of view MPA loaded MCM-41 are more uniformly dispersed as compared to TPA loaded MCM-41 while from proton conductivity point of view TPA loaded solid powders show promising performance as compared to MPA loaded in MCM-41. EDAX microanalysis carried out on solid powder samples reveals the presence of silicon and aluminum in pure MCM-41 as well as in heteropolyacids loaded MCM-41. Tungsten and molybdenum findings in pure TPA and MPA also support the presence of heteropolyacids in solid composite powders.

4. Conclusions

This study has demonstrated that promising solid proton conductors can be developed by loading heteropolyacids

(TPA and MPA) onto MCM-41 molecular sieve. The preparation procedure of the composite solids was optimized to ensure negligible leaching of the solid acids from the MCM-41 structure. The proton conductivity of the composite solids at room temperature was found to increase with the loadings of heteropolyacids, namely tungstophosphoric acid and molybdophosphoric acid and was strongly influenced with the presence of water. The characterization of composite solids by IR, XRD and SEM confirm the existence of Keggin anions in the MCM-41 structure, which contributes to high conductivity. Proton conductivity of composite powders increased to exceptionally high values at room temperature in hydrated conditions. Significant conductivities have been achieved with the increased water content up to 50 wt.% water. Leaching study carried out on the composite solids confirmed that the material leached out through the composites was negligible and hence almost complete loading of heteropolyacids into the MCM-41 structures was ensured. Since the conductivity in presence of water was found to be appreciably high, these newly developed solid proton conducting composites may also be used in developing highly proton conductive membranes for direct methanol fuel cells.

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