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AFM and SEM-EDS examination of highly dispersed heteropolyacids supported on MCM 41 and SBA 15 mesoporous materials

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Heteropolyacids (HPAs) $H_3PMo_{12}O_{40}$ (HPM) and $H_4PVMo_{11}O_{40}$ (HPVM) supported on mesoporous pure-silica and Al, Fe modified molecular sieve MCM-41 and SBA-15 have been prepared and characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM) with EDS.All supported HPAs were prepared by impregnation using the incipient wetness techniques with a mixture of water: ethanol = 1:1. AFM features show that nanoclusters of HPA-molecular sieves composites of various heights were formed on the surface. The morphology of the pure molecular sieves and HPA-molecular sieves composites surface, respectively, has an island-like structure. SEM studies confirmed the uniformity of the distribution of active phase in the supported samples. It is found that most of HPM and HPVM (active phases) in supported samples are well dispersed on all supports. HPAs supported on MCM-41 ans SBA-15 have still kept their Keggin structure.A relatively uniform distribution of active phase in the supports pores was confirmed by EDS analysis.

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1. Introduction

Heteropolyacids with Keggin structure have been widely investigated as catalysts in many acid and oxidation reactions both in the heterogeneous and homogeneous systems. In the catalysis application the disadvantages of pure HPAs used as catalysts are their very low surface area and nonporosity. In order to be more effective for catalytic reactions, HPAs are usually impregnated on different porous materials with high surface area and a proper pore system [1-11].

Among mesoporous molecular sieves the most studied material is MCM 41. It is a very interesting material for catalysis and as a support because it has a high thermal stability (up to 1198K), large surface area (over 700 m^2/g) and a good adsorption capacity for organic molecules [12-21]. By proper preparation method and reactants types, pore dimensions of MCM-41 can be produced in the range from 15 to 100Å, which allow the easy introduction of HPAs molecules (12 Å diameter).

SBA-15 is a relatively new discovered mesoporous molecular sieve with uniform tubular channels whose pore diameters can be produced in the range from 50 to 300 Å, which allow the easy introduction of HPAs molecules (12 Å diameter). Compared with MCM-41 molecular sieve, SBA-15 has larger pore diameters, thicker pore walls and higher hydrothermal stability [22-23].

In the literature very few references have been reported concerning $H_3[PMo_{12}O_{40}]$ and $H_4[PMo_{11}VO_{40}]$ supported on MCM41 mesoporous silicate, majority of the studies have been focused on investigation the most acidic HPAs in the series, namely $H_3PW_{12}O_{40}$.

The goal of this work was to characterise the texture and the structure by means of atomic force microscopy and scanning electron microscopy with EDS of these heteropolyacids supported on mesoporous materials.

2. Experimental

$H_4[PMo_{11}VO_{40}]\cdot 12H_2O$ was prepared by two methods: Tsigdinos and hydrothermal method [24-25]. In both cases HPVM was crystallized slowly from aqueous solution at room temperature. $H_3[PMo_{12}O_{40}]\cdot 13H_2O$ was purchased from Merck. The as-received material was recrystallized prior to use. HPAs are stable at room temperature with 12-14 H_2O molecules.

Mesoporous silica Si-MCM41 and modified MCM-41 molecular sieves were synthesized according to the procedure developed by Beck et al. [12]. Mesoporous silica SBA-15 was synthesized according to the procedure developed by D.Zhao et al. [22].

The HPA active phase deposition on Si-MCM41, Al-MCM-41 (Si/Al = 20), Fe-MCM41 (Si/Fe = 50), SBA 15 and Ti- SBA 15 (Si/Ti = 50) supports was performed by impregnation from water : ethanol = 1:1 solution. The HPM and HPVM acids were deposited in the concentration of 15 and 30 wt. % loading.

The structure and texture of HPM and HPVM supported on molecular sieves were studied by AFM and scanning electron microscopy with EDS analysis.

Surface morphology and the nanostructure of HPAs - molecular sieves composites were examined by means of an AFM instrument, AutoProbe CP Research, TM Microscope. All measurements were performed in noncontact mod (NCM) using a rectangular silicon cantilever. A typical spring constant of the cantilever is in the range 30-80 N/m and typical resonant frequency in the range of 250-300 kHz. The samples were pressed in pellets and than micrographs were recorded. For each sample, images of 2 × 2 μm, 5 × 5 μm and 10 × 10 μm were recorded. The calculations of AFM parameters were performed by software SPMLab NT Ver.6.0.2.

Microstructure characterisation of the catalyst particles was carried out with a JEOL JSM 6460 LV instrument equipped with an OXFORD INSTRUMENTS EDS analyser. Powder materials were deposited on adhesive tape fixed to specimen tabs and then ion sputter coated with gold.

3. Results and discussion

3.1 AFM measuring method

According to European BCR Project "Scanning tunnelling microscopy methods for roughness and micro hardness measurements" the roughness parameters are divided into four groups: amplitude, hybrid, functional and spatial properties [26]. The amplitude properties are described by six parameters, which give information about the statistical average properties, the shape of the height distribution histogram and about extreme properties. All the parameters are based on two-dimensional standards that are extended to three dimensions [26].

Table 1. Roughness amplitude parameters of molecular sieves and HPAs supported on molecular sieves.

Sample	Roughness amplitude parameters (2 × 2 μm)			
	Ra [nm]	RMS [nm]	Avg. height [nm]	Max. range [nm]
SBA-15	30.8	37.4	123.5	249.2
Si-MCM41	5.4	7.11	40.6	80.8
Fe-MCM41	5.8	7.5	44.3	67.0
Al-MCM41	6.7	8.6	33.3	73.7
15HPVM/SBA-15	12.9	16.2	65.4	114.9
15HPM/Si-MCM41	16.3	20.3	63.6	150.0
15HPVM/FeMCM41	18.4	23.0	83.9	159.7
15HPM/Al-MCM41	11.8	15.2	52.8	114.1

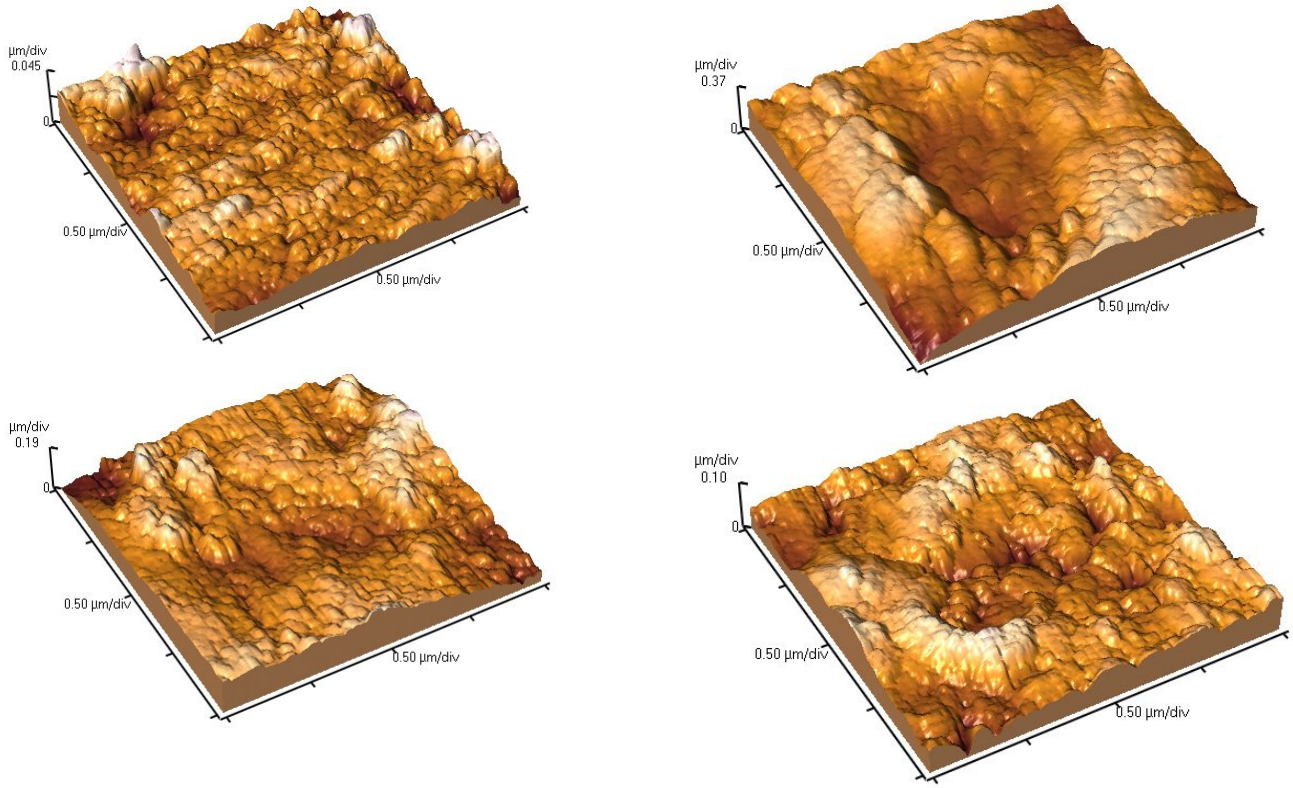


Fig. 1. 3D AFM images (2 × 2 μm) of Si-MCM41 (a), 15HPM/Si-MCM41 (b), SBA-15 (c) and 15 HPVM/SBA-15 composites (d).

The roughness average R_a is the arithmetic average of the absolute distances of the surface points from the mean plane. It is the most frequently used surface roughness parameter giving information about the statistical average properties and is defined as:

$$S_a = \frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left|z(x_k,y_l)-\mu\right| \quad (1)$$

where M is the number of columns in the surface, N is the number of rows in the surface and μ is the mean height:

$$\mu = \frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1} z(x_k, y_l) \quad (2)$$

Typically, AFM users rely on root mean square (RMS) roughness, S_q, as the measurement of choice.

$$S_q = \sqrt{\frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left[z(x_k,y_l)-\mu\right]^2} \quad (3)$$

where μ is the same mean value of the height, *z*, across all in-plane coordinates *(x,y)*.

AFM features show that nanoclusters of HPA-molecular sieves composites of various heights were formed on the surface (Fig. 1). The morphology of the pure molecular sieves and HPA-molecular sieves composites surface, respectively, has an island-like structure.

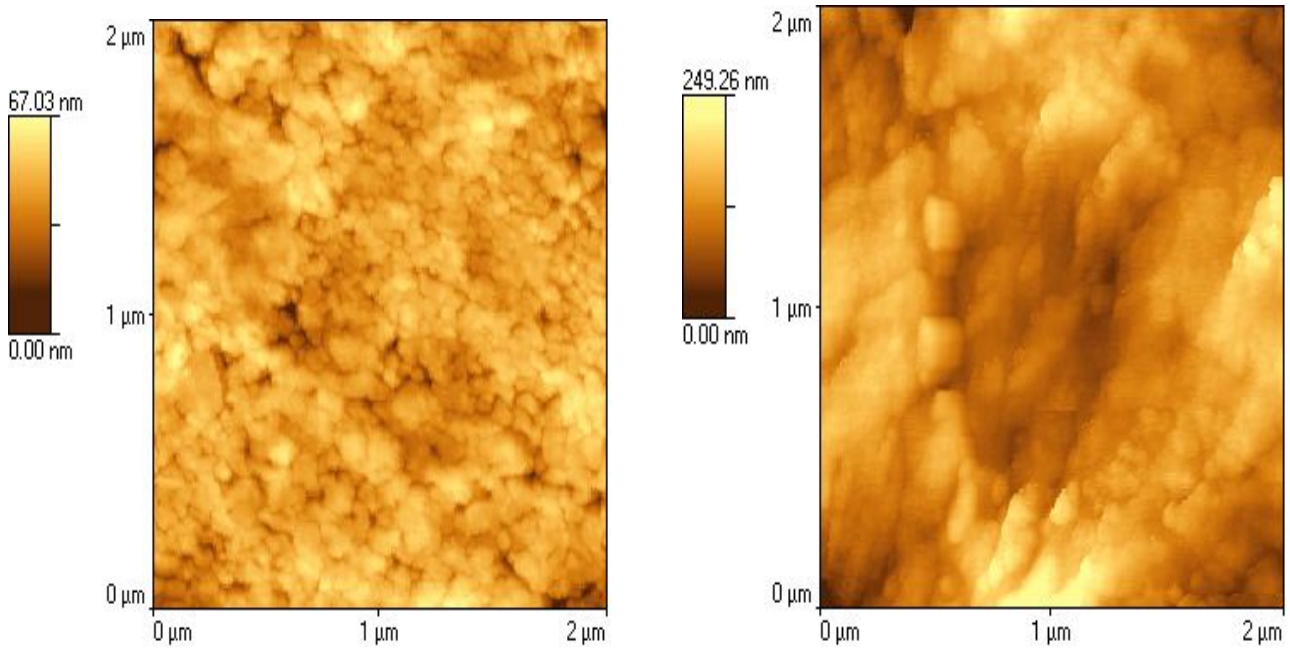


Fig. 2. 2D AFM images (2 x 2 µm) of Fe-MCM41 (a), and SBA-15 composites (b).

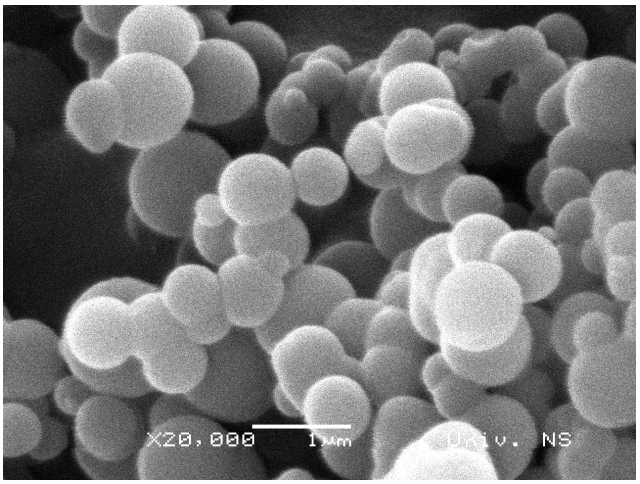
The smallest roughness values were observed for MCM-41 types molecular sieves: for Si-MCM-41, R_a = 5.4 nm (Table 1). AFM images reflect very well the surface roughness, as could be seen in Fig. 1 and Fig. 2.

The average height ranging from 33 nm for Al-MCM41 to 124 nm for SBA-15 molecular sieve, while for HPA-molecular sieves composites the average height values varying between 23 nm to 84 nm. (Table 1).

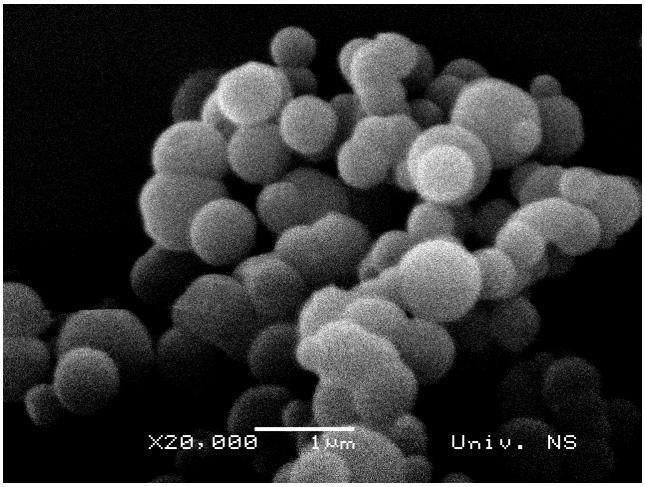
Cursor measurements indicate that nanoclusters of HPA-molecular sieves composites have the maximum range of their height varying from 67 nm (Fe-MCM41) to 249 nm (SBA-15) (Fig. 2). From the AFM images examination of Si-MCM41 surface, particle diameters between 50 and 100 nm were evidenced.

3.2 SEM-EDS method

Analysis of SEM images revealed that Si-MCM41 support is composed of clusters of regular shaped particles with an average diameter below 1 µm (Figure 3a). The surface morphology of Si-MCM41-supported HPAs is practically identical to that of the pure molecular sieve (Fig. 3b). From SEM images one can see that no separate crystallites of the bulk phase of HPAs were found in the supported samples.



a



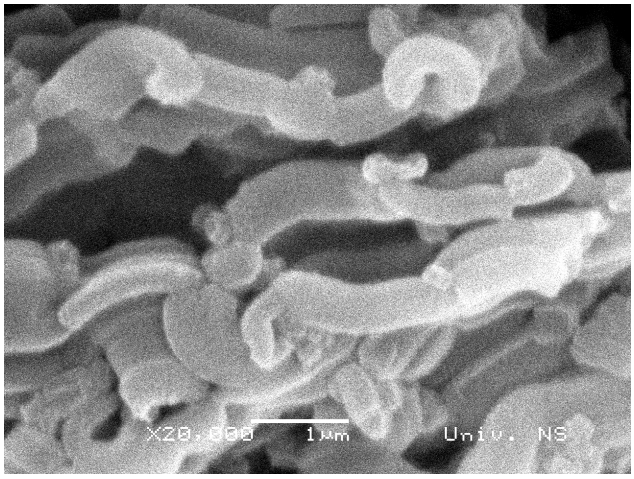
b

Fig. 3 SEM micrographs of Si-MCM41 (a) and HPM/ Si-MCM41 (b).

The morphology of SBA 15 support is composed of ropelike shaped particles with an average diameter below 1 μm (Fig. 4a). The diameter size of the ropes is relatively uniform, and the ropes can be aggregated into a wheatlike macroscopic structure.

The surface morphology of SBA 15-supported HPAs is practically identical to that of the pure molecular sieve (Figure 4b). As well as in the case of Si-MCM41-supported HPAs no separate crystallites of the bulk phase of HPAs were found in the supported samples.

HPAs distribution on supported samples surface was analysed by EDS method, which was performed as point analysis on thin particles. By this technique the content of silicon from Si-MCM41, silicon and aluminium from Al-MCM41, silicon and iron from Fe-MCM41 and Mo, V and P elements of heteropolyacid was determined (Table 2). The EDS point analysis was made over several domains with 10x10 μm dimensions on the same sample. The analysis was repeated on different samples in order to ensure the reproducibility of the obtained results.



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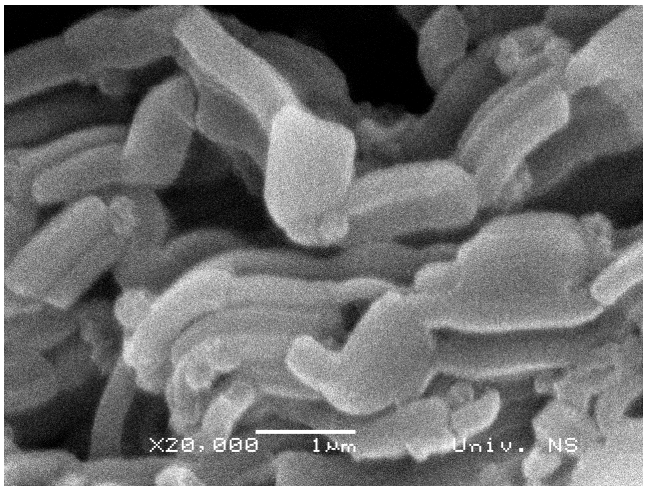

b

Fig. 4. SEM micrographs of SBA 15 (a) and HPM/SBA 15 (b)

Microanalitycal data of EDS analysis show that the molybdenum and phosphorous (15 wt.% HPM/Si (Al, Fe)-MCM41) and molybdenum, phosphorous and vanadium (15 wt.% HPVM/Si (Al, Fe)-MCM41) contents are homogeneous and close to stoichiometric values.

Table 2 . Elemental analysis (wt.%) by EDS method of HPAs supported on molecular sieves.

Sample	Elemental analysis (wt.%)					
	Mo		P		V	
	exp.	stoich.	exp.	stoich.	exp.	stoich.
15HPM /SBA-15	10.4	9.5	0.31	0.25	-	-
15HPVM /SBA-15	9.4	8.9	0.28	0.26	0.39	0.42
30HPM /Ti-SBA-15	17.1	18.9	0.37	0.50	-	-
30HPVM /Ti-SBA-15	17.3	17.8	0.49	0.52	0.85	0.86
15HPM/Si-MCM41	9.3	9.5	0.29	0.25	-	-
15HPVM/Si-MCM41	9.2	8.9	0.24	0.26	0.45	0.42
15HPM/FeMCM41	9.1	9.5	0.21	0.25	-	-
15HPVM/FeMCM41	8.4	8.9	0.32	0.26	0.25	0.42
30HPM/FeMCM41	17.8	18.9	0.42	0.50	-	-
30HPVM/FeMCM41	16.8	17.8	0.45	0.52	0.79	0.86
15HPM/Al-MCM41	8.8	9.5	0.28	0.25	-	-
15HPVM/Al-MCM41	9.1	8.9	0.28	0.26	0.35	0.42

In the case of Al-MCM41 supported HPM the content of Mo is 8.8 % wt. (stoichiometric value is 9.5), while P content is 0.28 (stoichiometric value is 0.25) (Table 2 and Figure 5 b). For Al-MCM41 supported HPVM the content of Mo is 9.1 % wt. (stoichiometric value 8.9), P content is 0.28 (stoichiometric value is 0.26) and V content is 0.35 (stoichiometric value is 0.42).

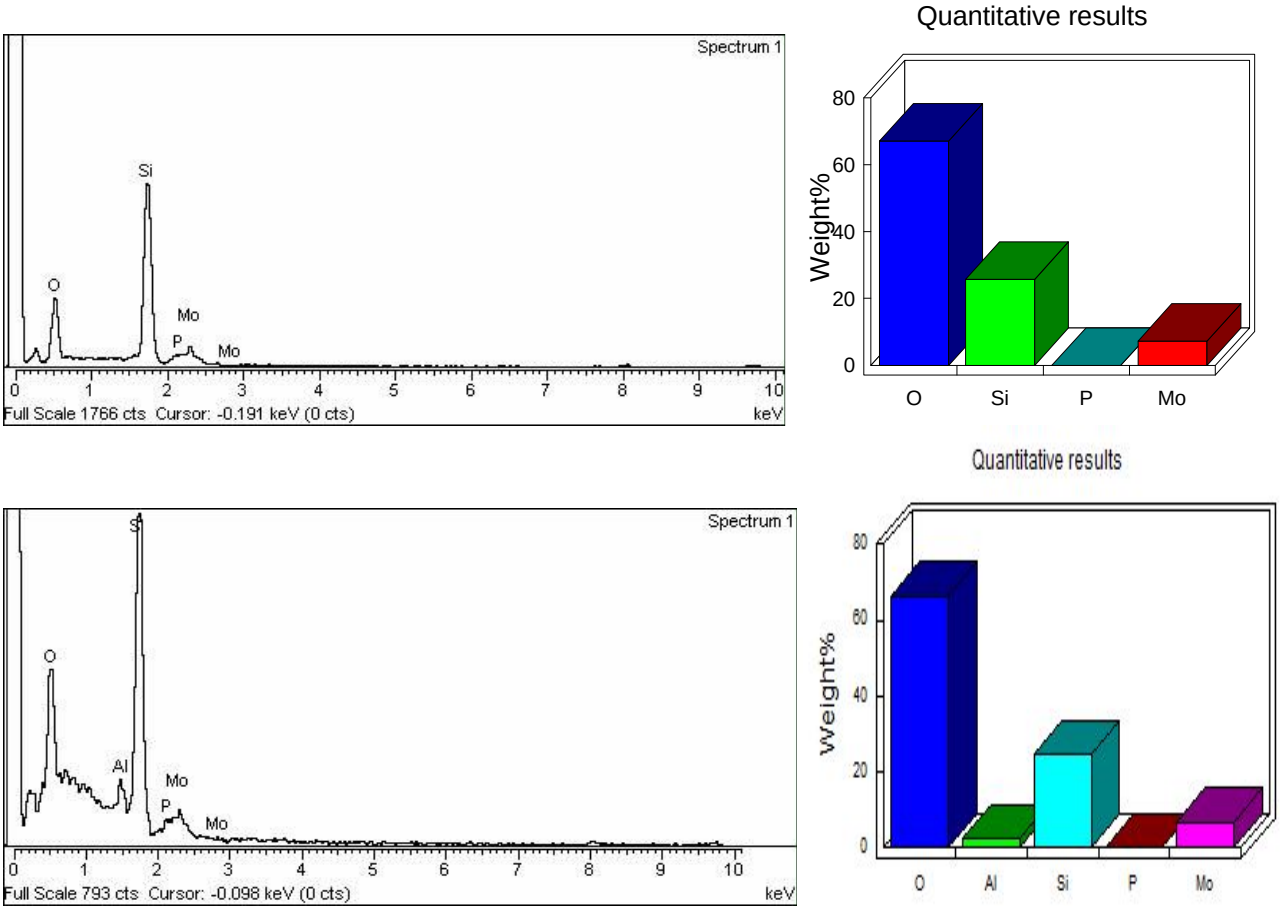

Fig. 5. a, b Microanalytical data of a 10x10 μm area and quantitative results of 15HPM/Si-MCM41 (a) and 15HPM/Al-MCM41 (b)

EDS analysis of Fe-MCM41 supported HPM (30 wt. %) shows that the concentration of Mo is 17.8 wt. % (stoichiometric value is 18.9), while the P content is 0.42 wt. % (stoichiometric value is 0.50) (Table 2). It could be

observed that 30HPM/ Fe-MCM41 exhibits a higher deviation of Mo and P concentration values from the stoichiometric ones, probably owing to higher active phase concentration supported at the surface of molecular sieve.

By the same EDS technique were obtained the chemical compositions of silicon from SBA-15, silicon and titanium from Ti-SBA-15 and Mo, V and P elements of heteropolyacid.

Microanalitycal data of EDS analysis show that the molybdenum and phosphorous (15 wt.% HPM/ SBA-15) and molybdenum, phosphorous and vanadium (15 wt.% HPVM/ SBA-15) contents are homogeneous and close to stoichiometric values.

In the case of SBA-15 supported HPM the content of Mo as % wt. is 10.4 (stoichiometric value is 9.5), while P content is 0.31 (stoichiometric value is 0.25). For SBA-15 supported HPVM the content of Mo as % wt. is 9.36 (stoichiometric value 8.9), P content is 0.28 (stoichiometric value is 0.26) and V content is 0.39 (stoichiometric value is 0.42) (Table 2).

EDS analysis of Ti-SBA15 supported HPM (30 wt. %) shows that the concentration of Mo is 17.11 wt. % (stoichiometric value is 18.9), while the P content is 0.37 wt. % (stoichiometric value is 0.50). It could be observed that 30HPM/Ti-SBA15 exhibits a higher deviation of Mo and V concentration values from the stoichiometric ones, probably owing to higher active phase concentration supported at the surface of molecular sieve.

4. Conclusions

HPAs anions preserved their Keggin structure on the MCM-41 and SBA-15 surface and they are finely dispersed over the support.

AFM features show that nanoclusters of HPA-molecular sieves composites of various heights were formed on the surface. The morphology of the pure molecular sieves and HPA-molecular sieves composites surface, respectively, has an island-like structure. The average height ranging from 33 nm for Al-MCM41 to 124 nm for SBA-15 molecular sieve, while for HPA-molecular sieves composites the average height values varying between 23 nm to 84 nm**.**

The data of EDS analysis show that the molybdenum and phosphorous (HPM/SBA-15 and HPM/MCM41) and molybdenum, phosphorous and vanadium (HPVM/SBA-15 and HPVM/ MCM41) contents are close to stoichiometric values and that HPAs are homogeneously dispersed over the support surface.

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