

## PHYSICO-CHEMICAL FEATURES OF SOME KEGGIN TYPE HETEROPOLYACIDS SUPPORTED ON SILICA AND TITANIA

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### ABSTRACT

*The structure and texture of  $H_3PMo_{12}O_{40}$  (HPM) and  $H_4PVMo_{11}O_{40}$  (HPVM) supported on silica (Aerosil- Degussa and Romsil types) and titania are studied by XRD, FT-IR, low temperature nitrogen adsorption and scanning electron microscopy*

*All supported heteropolyacids were prepared by impregnation using the incipient wetness techniques with a mixture water: ethanol = 1:1. In order to obtain highly dispersed HPA species, the samples were prepared with different quantities of active compounds: 5-40 wt. %. The effect of loading on textural and structural properties was examined for supported HPA catalysts comparatively with parent acids and their mechanical mixtures. It is found that most of HPM and HPVM (active phases) in samples are well dispersed on the support and both silica and titania supported HPA still keeps its Keggin structure.*

*The surface morphology of the silica and titania supported samples is almost similar to that of support, and thereby a relatively uniform distribution of active phase in the support pores are expected.*

*The dispersion of active phase on support was estimated from XRD pattern, and it decreases with acid content. FTIR spectra of mechanical mixtures of HPA with silica are similar to the supported samples, so this method cannot distinguish these materials. Contrasting with supported HPA on silica, their mechanical mixtures exhibit sharp and narrower diffraction lines, more similar to crystalline pure HPA.*

### KEYWORDS:

heteropolyacids, silica, titania, texture, structure, BET, XRD

### 1. INTRODUCTION

Keggin type heteropolyacids (HPA) have been widely used in acid-catalysed reactions as well as oxidation reactions both in the heterogeneous and homogeneous systems [1-7]. Heteropolyacids have been pointed out lately as versatile green catalysts for a variety of reactions: alkylation and acylation of aromatics, esterification, liquid biphasic processes [8-9]. There is an interest to substitute liquid catalysts (e.g.  $H_2SO_4$ , HF, p-toluenesulphonic acid) – which are corrosive, toxic and difficult to separate from reaction solution- by more environmentally friendly solid acids. Among many possible forms of heteropolyacids used as catalysts, there are their salts and supported heteropolyanions [10-17].

Pure HPA generally show low catalytic reactivity owing to their small surface area. In order to be more effective for catalytic reactions, HPA are usually impregnated on different porous materials. The type of carrier, textural and structural properties influence the thermal stability and the catalytic activity of Keggin-type heteropolyacids.

In order to obtain highly dispersed heteropolyacids species,  $H_3PMo_{12}O_{40}$  and  $H_4PVMo_{11}O_{40}$  were supported on various supports: silica (Aerosil- Degussa and Romsil types) and titania. The goal of this work was to characterise the texture and structure of these heteropolyacids supported on silica and titania in reference to the bulk solid acids and their mechanical mixtures.

## 2. EXPERIMENTAL

$H_4 [PMo_{11}VO_{40}] \cdot 12H_2O$  was prepared by two methods: Tsigdinos and hydrothermal method.  $H_3[PMo_{12}O_{40}] \cdot 13H_2O$  was purchased from Merck. The as-received material was recrystallized prior to use. In the present work three types of supports were used: silica (Aerosil- Degussa and Romsil types) and  $TiO_2$ . HPM and HPVM heteropolyacids were deposited by impregnation in the amount varying from 10 to 40 % loading (denoted for example 30HPM/ $SiO_2$ ), depending of support type.

Textural characteristics of the outgassed samples were obtained from nitrogen physisorption using a Micrometrics ASAP 2000 instrument. The specific surface area  $S_{BET}$ , mean cylindrical pore diameters  $d_p$  and adsorption pore volume  $V_{pN_2}$  were determined. Prior to the measurements the samples were degassed to  $10^{-5} Pa$  at  $150^\circ C$ . The BET specific surface area was calculated by using the standard Brunauer, Emmett and Teller method on the basis of the adsorption data. The pore size distributions were calculated applying the Barrett-Joyner-Halenda (BJH) method to the desorption branches of the isotherms. The IUPAC classification of pores and isotherms were used in this study.

Microstructure characterisation of the catalyst particles was carried out with a Jeol JSM 6460 LV instrument equipped with an EDX analyser. Powder materials were deposited on adhesive tape fixed to a glass slide and then coated with gold to form a thin film.

Powder X-ray diffraction data were obtained with a XR Fischer diffractometer using the  $Cu K_\alpha$  radiation in the range  $2\theta = 5 \div 60^\circ$ .

The IR absorption spectra were recorded with a Biorad FTS 60A spectrometer (spectral range  $4000-200\text{ cm}^{-1}$  range, 256 scans, and resolution  $2\text{ cm}^{-1}$ ) using KBr pellets.

## 3. RESULTS AND DISCUSSION

The nitrogen adsorption isotherms of heteropolyacids supported on Romsil, Aerosil and titania are shown in Figures 1a, 2a and 3a. For 30HPVM/Romsil we observe a type IV isotherm with a type H1 hysteresis loop in the high range of relative pressure. For the values of relative pressure higher than 0.8 condensation take place giving a sharp adsorption volume increase. This behavior indicates that this sample has a

mesoporous character. Hysteresis loop type shows that HPVM/Romsil sample consists of agglomerates or compacts of approximately uniform spheres in fairly regular array. Both HPM and HPVM heteropolyacids supported on Romsil present the type IV isotherm with a type H1 hysteresis loop.

The adsorption-desorption isotherms of nitrogen for HPM and HPVM supported on Aerosil, present also type-IV isotherm with a type H1 hysteresis loop in the 0.85-1 range of relative pressure (Figure 2a). The shape of desorption branch of isotherms for Aerosil supported samples is a little different than Romsil supported ones.

For titania supported HPA the adsorption-desorption isotherms show a type H3 hysteresis loop in the middle range of  $P/P_0$  characteristic for aggregates of plate-like particles forming slit-shaped pores (Figure 3a).

The pore size distributions were calculated by Barret-Joyner-Halenda (BJH) method applied to the desorption branches of the isotherms. BJH method is further used to check and to complete the previous results. The pore size distribution curve of 30HPVM supported on Romsil and Aerosil show a maximum at 25-26 nm (Figure 1b, 2b). Pores with sizes belonging to the entire range characteristic for mesoporosity (2-50 nm) and little macroporosity appear for HPA supported on both types of silica at loading varying from 10wt.% to 30wt.%. The shape of pore size distribution curves of HPA/Romsil is broad and asymmetric, the size of pores being from 10 nm to 80 nm. The pore size distribution curves of HPA/Romsil are broader than HPA/Aerosil ones, especially in the macroporosity range, showing a nonuniformity of the porous structure. The pore size distribution curves of both HPA supported on titania are completely different showing two maximums at 1.64 nm (microporosity range) and 3.56 nm (mesoporosity range).

The specific surface areas of used supports are 90 m<sup>2</sup>/g for silica-Romsil, 235 m<sup>2</sup>/g for silica-Aerosil and 325 m<sup>2</sup>/g for titania [17]. The specific surface areas of HPA deposited on all supports decreased with active phase concentration (Table I). Thus, the specific surface area of silica Aerosil supported heteropolyacids decreased from 235 m<sup>2</sup>/g for Aerosil support to 140.7 m<sup>2</sup>/g for 20HPM/Aerosil sample, respectively to 153 m<sup>2</sup>/g for the 20 HPVM/Aerosil sample. In addition, the specific surface area decreased drastically from 325 m<sup>2</sup>/g (TiO<sub>2</sub> support) to 248.4 m<sup>2</sup>/g for 20 HPVM/TiO<sub>2</sub> and to 115.9 m<sup>2</sup>/g for 40 HPVM/TiO<sub>2</sub>, respectively.

Specific surface area diminution could be explain owing to support pores blocking by active phase, as well as by the formation of some HPA crystallites agglomeration (especially at high loading of active phase). As a large percentage of pores of titania supported HPA are micropores (below 2 nm) and the Keggin unit diameter is ca. 12Å, it stand to reason that micropores are blocked by active phase and the specific surface area drops drastically by increasing the active phase loading.

The mean pore diameter varies between 2.8-26 nm for Romsil supported HPA, 20-28 nm for Aerosil supported HPA and 1.2-4.7 nm for titania supported HPA in function of different surface coverage, as it results from the pores size distribution curves. For all loading, both HPA

exhibit differential pore size distribution in the mesoporosity range and with only little macroporosity for silica supported samples, and pore size distribution in the microporosity and mesoporosity range for titania supported samples.

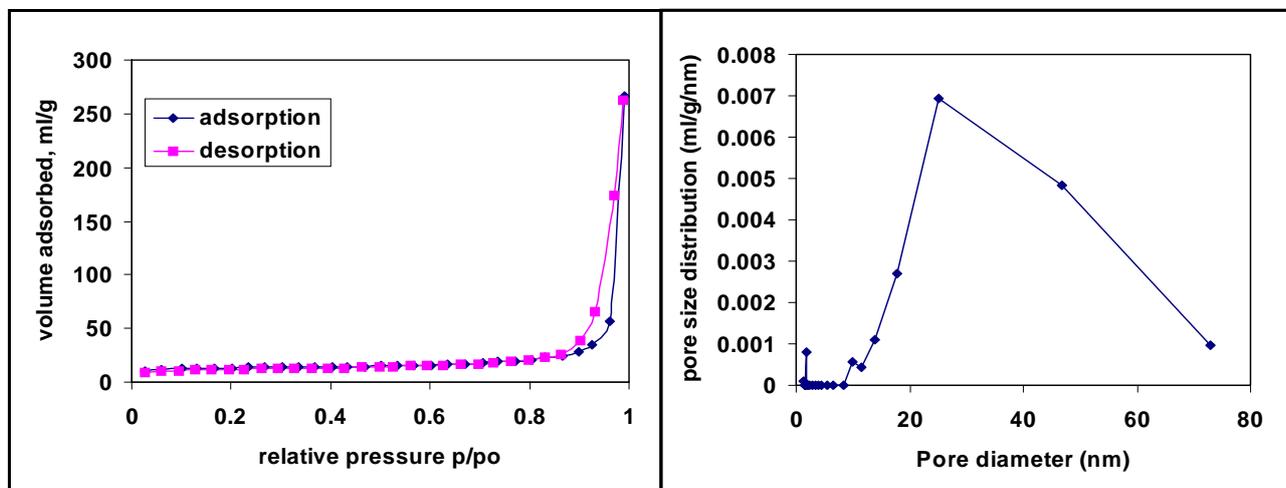


Figure 1 Nitrogen adsorption-desorption isotherms at 77 K (a) and pore size distribution derived from the desorption branch of nitrogen physisorption (b) of 30HPVM supported on Romsil

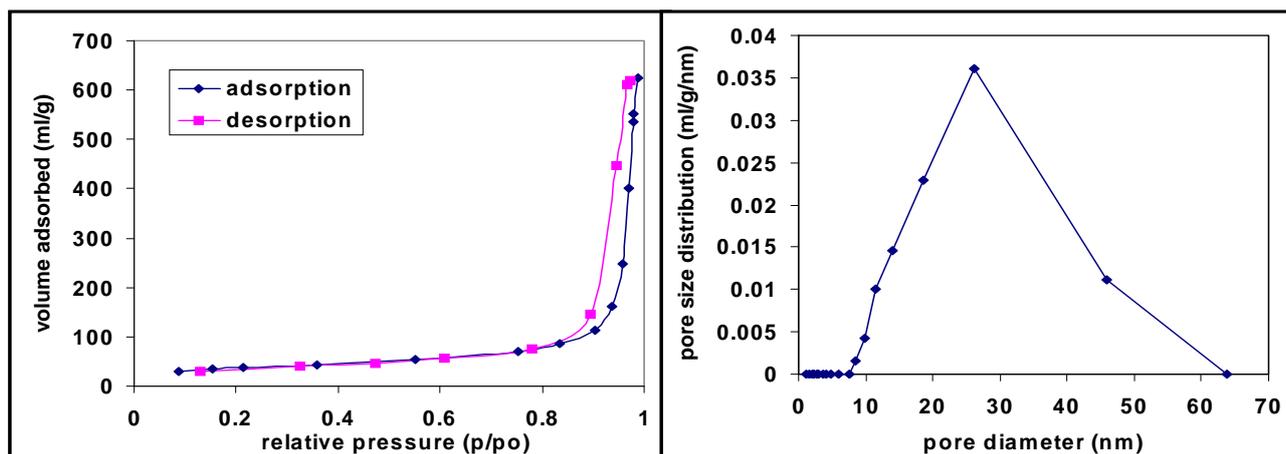


Figure 2 Nitrogen adsorption-desorption isotherms at 77 K (a) and pore size distribution derived from the desorption branch of nitrogen physisorption (b) of 30HPVM supported on Aerosil

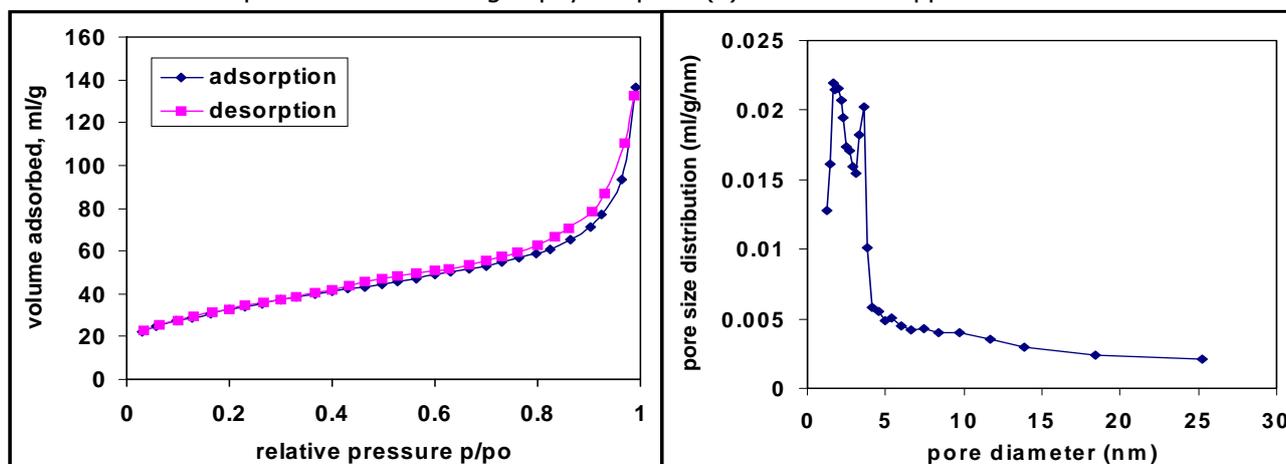


Figure 3 Nitrogen adsorption-desorption isotherms at 77 K (a) and pore size distribution derived from the desorption branch of nitrogen physisorption (b) of 40HPVM supported on titania

In order to confirm the presence of the Keggin anion on silica and titania respectively, the supported HPA samples were analysed by FTIR. The  $\text{PMo}_{12}\text{O}_{40}^{3-}$  Keggin ion structure consists of a  $\text{PO}_4$  tetrahedron surround by four  $\text{Mo}_3\text{O}_{13}$  formed by edge-sharing octahedra. These groups are connected each other by corner-sharing oxygen. This structure give rise to four types of oxygen, being responsible for the fingerprints bands of Keggin ion between  $1200$  and  $700\text{ cm}^{-1}$ .

The pure HPA show an IR spectrum with the specific lines of the Keggin structure containing the main absorption lines at  $1064\text{ cm}^{-1}$ ,  $960\text{ cm}^{-1}$ - $965\text{ cm}^{-1}$ ,  $864\text{ cm}^{-1}$ - $868\text{ cm}^{-1}$ ,  $784\text{ cm}^{-1}$  - $804\text{ cm}^{-1}$  assigned to the stretching vibrations  $\nu_{\text{as}}\text{ P-O}$ ,  $\nu_{\text{as}}\text{ Mo=O}_t$ ,  $\nu_{\text{as}}\text{ Mo-O}_c\text{-Mo}$  and  $\nu_{\text{as}}\text{ Mo-O}_e\text{-Mo}$  [9, 10]. These bands are preserved on the supported samples, but they are broadened and partially obscured because of the strong absorption bands of silica ( $1100$ ,  $800$  and  $470\text{ cm}^{-1}$ ). The replacing of a Mo atom with a V one leads to the appearance of two "shoulders" corresponding to the absorption maxim of the vibration  $\nu_{\text{as}}(\text{P-O}_p)$  at  $1080\text{ cm}^{-1}$  and  $\nu_{\text{as}}(\text{V-O}_T)$  at  $980\text{ cm}^{-1}$ . This confirms the presence of  $\text{V}^{5+}$  inside the  $\text{MO}_6$  octahedral. These shoulders could not be seen in the IR spectra of supported HPA as adsorption bands of silica overlap them completely.

On the other hand, FTIR spectra of mechanical mixtures of HPA (HPM, HPVM) and silica (Romsil, Aerosol) or titania on the same loading range have shown similar characteristics with supported samples. Thus, FTIR method cannot distinguish unequivocally the difference between supported HPA and mechanical mixtures with silica and titania, respectively.

XRD patterns of various Romsil silica-supported HPM and HPVM samples with different loading are illustrated in Figure 4 and 5 respectively. XRD patterns were obtained in order to be sure HPM and HPVM were effectively supported on silica, and to evaluate the dispersion state of the acid on support. Amorphous silica gel display only a broad band centred at  $2\theta = 22^\circ$ . It may be observed that some of the diffraction peaks characteristic of crystalline HPA appeared on the supported catalysts. For samples with 10 wt.% loading, XRD has shown larger peak at  $2\theta = 22^\circ$  attributed to silica, but typical peaks of pure HPA were not observed. For samples with 20 wt.% HPVM loading, two very weak diffraction peaks characteristic of active phase can be seen around  $2\theta = 7.8^\circ$  and  $8.7^\circ$ , while in the case of 20HPM/Romsil one weak peak are observed at  $2\theta = 7.8^\circ$ . The peaks become not only more evident on intensity, but also less broad (in comparison with pure HPA pattern) as the concentration of active phase increases.

Contrasting with supported HPA on Romsil silica, mechanical mixtures of the acid with  $\text{SiO}_2$  exhibit sharper and narrower diffraction lines more similar to crystalline HPM and HPVM respectively. In order to make this comparison, XRD of the 30 wt.% HPM and 30 wt.% HPVM supported on Romsil and their mechanical mixtures with identical mass of HPA were obtained. The results displayed on Figure 4 and 5 show that the diffraction lines produced by mechanical mixtures resembles the pure crystalline HPM

and HPVM. The characteristic reflections of HPM and HPVM present higher intensities and are less broad than the supported samples. XRD for supported HPA is distinctive of mechanical mixtures of these solids, and therefore can be used to characterise these catalysts.

Table I Characteristic parameters of the texture of pure and supported HPA samples

Sample	Surface area (m <sup>2</sup> /g)	Pore volume, V <sub>IP</sub> (cm <sup>3</sup> /g)	Pore diameter, d <sub>m</sub> (nm)
HPM	3.53	0.011	14.08
HPVM	3.89	0.012	12.66
10HPM/Romsil	75.0	0.40	2.76
20HPM/Romsil	66.9	0.36	11.1
30HPM/Romsil	63.2	0.38	25.1
10HPVM/Romsil	78.4	0.12	3.77
20HPVM/Romsil	64.9	0.57	25.9
30HPVM/Romsil	62.9	0.41	25.4
20HPM/Aerosil	140.7	0.98	27.9
30HPM/Aerosil	132.5	0.83	25.0
40HPM/Aerosil	103.8	0.67	25.7
20HPVM/Aerosil	153.0	0.86	22.7
30HPVM/Aerosil	139.8	0.78	21.8
40HPVM/Aerosil	112.1	0.62	20.4
20HPM/TiO <sub>2</sub>	240.2	0.28	4.66
30HPM/TiO <sub>2</sub>	165.8	0.22	4.12
40HPM/TiO <sub>2</sub>	85.8	0.14	1.23
20HPVM/TiO <sub>2</sub>	248.4	0.29	4.51
30HPVM/TiO <sub>2</sub>	182.4	0.24	3.91
40HPVM/TiO <sub>2</sub>	115.9	0.21	1.64

In order to estimate the dispersion of active phase on silica support, the mean crystallite size has been calculated by Scherrer's equation [9] from the XRD patterns of the catalysts:

$$s_m = \frac{0.9\lambda}{B \cos \theta_B} \quad (1)$$

where  $s_m$  is the particle size,  $B$  is the full width at half maximum (in  $2\theta$ ) and  $\theta_B$  is the Bragg angle. The equation was applied to each sample using  $2\theta = 7.8^\circ$ , which is less influenced by the diffracted broad band of non-crystalline silica. The mean diameters of the HPM crystallites were 14.1, 15.6, 17.7 nm for the supported HPM/silica with 10, 20, 30 wt.% acid loading and 26.5 nm for 30HPM+silica mechanical mixture. In the case of HPVM, the mean diameters of crystallites were 12.9, 14.0, 17.7 nm for the supported HPVM/SiO<sub>2</sub> with 10, 20, 30 wt.% acid loading and 22.1 nm for 30HPVM+silica mechanical mixture.

By using the same Scherrer equation, the main diameter of HPM and HPVM was 32 nm; therefore, higher dispersion of heteropolyacids clusters is achieved on supported catalysts. These data indicate a decrease of HPM and HPVM dispersion when increasing acid loading, which is expected based on formation of larger agglomerates on silica surface with concentration of acid impregnated on the support.

The patterns of both HPA/TiO<sub>2</sub>, which were recorded after drying at 120°C, shows the main peaks characteristic of titania support, and only at small angles (5-10°) some weak peaks corresponding to heteropolyacids could be observed. Therefore, the XRD data indicate that for amount of

HPA corresponding to theoretical monolayer, small quantities of HPA crystallites are observed for titania-supported HPA. So, at relatively high concentration of active phase (40% wt%) some HPA molecules could not access to the support mesopores and crystallize as separate phases.

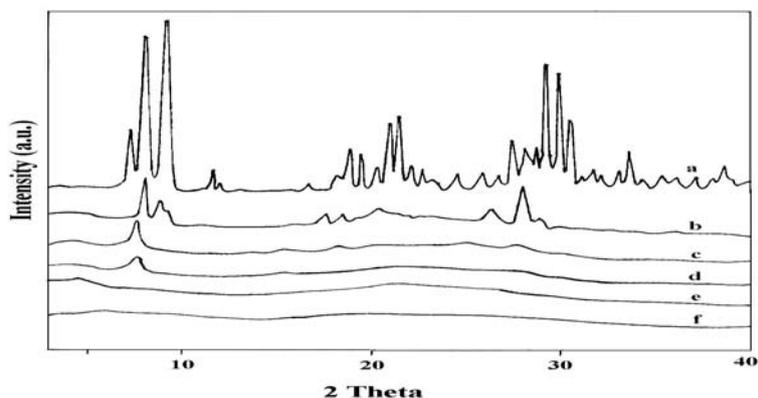


Figure 4 XRD patterns of: a)  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ; b) 30 wt.% HPM +  $\text{SiO}_2$  mechanical mixture; c) 30 HPM/ $\text{SiO}_2$ ; d) 20 HPM/ $\text{SiO}_2$ ; e) 10 HPM/ $\text{SiO}_2$ ; f)  $\text{SiO}_2$ -Romsil

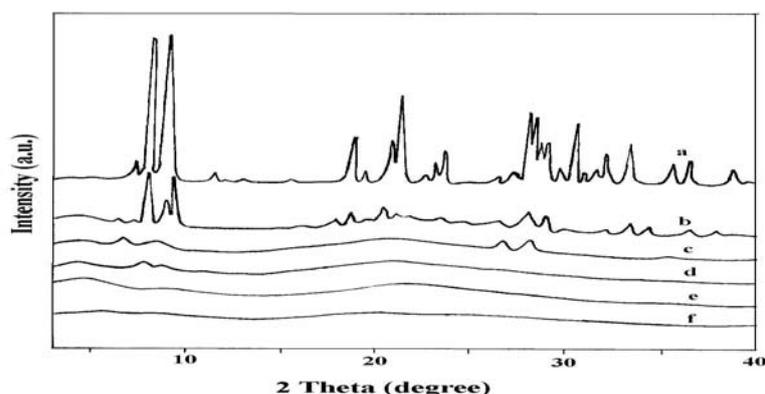


Figure 5 XRD patterns of: a)  $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ ; b) 30 wt.% HPVM +  $\text{SiO}_2$  mechanical mixture; c) 30 HPVM/ $\text{SiO}_2$ ; d) 20 HPVM/ $\text{SiO}_2$ ; e) 10 HPVM/ $\text{SiO}_2$ ; f)  $\text{SiO}_2$ -Romsil

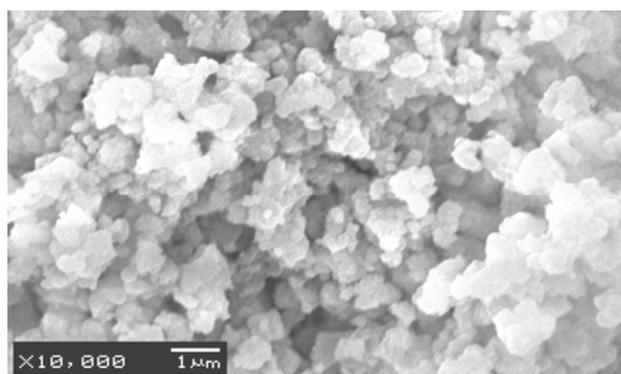


Figure 6. SEM micrographs of 30HPVM/Romsil

Silica Romsil support is composed of agglomerates of spherical particles with an average diameter below 1  $\mu\text{m}$  (Figure 6). The surface morphology of silica-supported HPA is practically identical to that of the pure silica. From SEM images one can see that no separate crystallites of the bulk phase of HPA were found in the supported samples. The surface of the titania supported HPA is composed of agglomerates of irregular shape particles with diameter of 100-200 nm.

#### 4. CONCLUSIONS

Different HPA loading has a strong impact on the texture and structure of silica and titania supported 12-molybdophosphoric and 1-vanado 11-molybdophosphoric acids. As indicated by FTIR and XRD results, silica-supported and titania-supported HPA still keeps its Keggin structure. For all loading, both HPA exhibit differential pore size distribution in the mesoporosity range and with only little macroporosity for silica supported samples, and pore size distribution in the microporosity and mesoporosity range for titania supported samples.

The higher dispersion of HPM and HPVM is confirmed by size of crystallites supported on silica determined by XRD. In addition, XRD patterns can differentiate supported samples from mechanical mixtures of heteropolyacids and silica, which cannot be evidenced by FTIR. A relatively uniform distribution of HPA on the support surface is observed for all compositions of active phase. No separate crystallites of the bulk phase of HPA were found in the SEM images of supported samples.

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