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Incorporation of 12-Tungstophosphoric acid in Titania spheres and fabrication of core-shell Polyoxotungstate/Titania nanostructures

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ABSTRACT

Core-shell 12-tungstophosphoric acid/TiO_2 (HPW/TiO_2) nanoparticles at 10 and 20% of HPW have been synthesized by simple in-situ sol- gel method. Characterization of the samples was carried out by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared (FTIR). The X-ray diffraction patterns of as prepared solid samples, indicated characteristic peaks of titania with additional peaks concerning to HPW in a very low intensities. This result in addition to the FTIR and SEM - EDX analysis data confirmed incorporation of HPW / TiO_2 nanostructure in spherical morphology with a particle size of around 25 nm.

Keywords: *Polyoxometalates; Phosphotungstic acid; Keggin type structure; Inorganic-inorganic nanostructure; Titania phase*.

INTRODUCTION

Polyoxometalates (POMs) are a large class of compounds that have been extensively used as acid and oxidation catalysts in many reactions, notably because their acid-base and redox properties that can be tuned by simple change in the polyanion chemical composition [1-4]. Among the numerous POMs, Keggin type POMs such as polyoxotungstates (PW) have been attractive because of their strong bronsted acid properties, exhibition of fast reversible multi electron redox behavior under mild conditions, tunable redox properties and also easy access [5]. Unfortunately, these compounds are highly soluble in various polar solvents which cause problems in separation from reaction media and render them less attractive for applications in heterogeneous catalysis. Among the different protocols proposed to solve problem, immobilization of polyoxometalates on porous oxide materials seems very cheap, attractive and practicable [6, 7].

To date, it has been shown that supporting POMs into the suitable inorganic solids such as carbon, silica, titania and etc [7-9] have good supporting properties which are effective method to overcome the mentioned problem [10-14]. In this work, successful preparation and characterization of polyoxotungstate nanostructure incorporated with TiO_2 (HPW/TiO_2) have been reported.

EXPERIMENTAL

Material and characterization

All chemicals and solvents were purchased from Merck or Fluka and used as received without further purification. Samples were characterized with FTIR, UV-Vis, SEM and X-ray powder diffraction. The secondary electron micrographs of the samples were obtained to obtain the shape and diameter of particles by scanning electron microscopy (SEM), using Philips Model 505 equipment, at a working potential of 15 kV, and samples coated with gold. Crystalline phase characterization was carried out by the powder X-ray diffraction (XRD) patterns were collected on Rigaku Miniflex diffractometer using Cu Ka radiation (λ = 0.1541 nm, k=0.94), nickel filter, in the high voltage source *40 kV, 30 mA*, and scanning angle between $2\theta = 10 - 90^{o}$ at a scanning rate of 18/min. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet spectrometer using KBr disc method in the 400–4000 cm−1 wavenumber range. The UV–vis spectra were recorded in the 400–4000 nm range on a Perkin-Elmer Lambda 35 apparatus.

Nanomaterials synthesis

- ***Synthesis of $nTiO_2$***

Titanium tetraisopropoxide (TTIP) (0.0125 mol) was added dropwise to a molar mixture of EtOH/H_2O and stirred vigorously at room temperature. The sol sample obtained by the hydrolysis process was then irradiated with ultrasonic equipment in an ultrasonic cleaning bath for 1 h and aged in closed beaker at room temperature for 24 h in order to obtain further hydrolyze of TTIP and mono dispersed TiO_2 nanoparticles. The sample obtained was finally dried at 100 ◦C for about 8 h in air to vaporize water and alcohol from the gel and grounded to the fine powder after calcination at 400 ◦C in air for 1h.

- ***Synthesis of PW nanoparticles***

Sodium tungstate (0.305mol) and disodiumphosphate (0.09 mol) were dissolved in boiling water (150 ml) and stirred magnetically. A concentrated hydrochloric acid (80 ml) was then added drop wise to the solution obtained and cooled. To separate impurity from the solution, some amount of ether was added and the lower part of solution was separated and evaporated to dryness mildly heating under air current.

- ***Synthesis of PW / TiO_2 nanocomposite (First attempt (FA))***

The core shell PW-TiO_2 nanopowders was synthesized on the basis of sol–gel method reported in literature for preparation of some titania supported PW nanoparticles [15]. A solution of tetrabuthyl orthotitanate in n-BuOH (25 mL) was prepared and stirred at 80 ºC. The mixture was then slowly cooled to room temperature and adjusted to pH= 2 by using hydrochloric acid and was added a solution containing sodium tungstate (0.305 mole) and disodiumphosphate (0.09 mole). The mixture was then maintained under constant stirring rate for 3 h until occurrence of gelling process. The gel obtained was filtered and dried in air at 100 ºC for 24 h and finally calcined in vacuum at 350 ºC for 4 h to fasten the titania network and washed with hot water (80 ºC) three times.

- ***Synthesis of HPW/TiO_2 nanocomposite (Direct synthesis method)***

- Synthesis of HPW/TiO_2 nanocomposite (Second Attempt (SA))

Suitable amount of Sodium tungstate dihydrate and disodium hydrogen phosphate dodecahydrate were added to 75 ml of DI water and the mixture was stirred at 80 ◦C for 1 h. Then appropriate amount of nano TiO_2 ($nTiO_2$) (in 10 and 20 wt %) were added to solution. After then the mixture was stirred at 80 ◦C for 9 h and 82 ml of HCl solution was added drop wisely and mixed for 3 h at 80 ◦C. The precipitate was separated from mixture after 3 h at room temperature and then poured into petri dish and placed in convection oven overnight at 100 ◦C. afterward the powder

was ground to fine particles and dried at 130 ◦C for 6 h in oven.

- Synthesis of HPW/TiO_2 nanocomposite (Third attempt (TA))

Suitable amount of disodium hydrogenphosphate dodecahydrate and nano TiO_2 for 10 and 20 %wt were added to 75 ml of DI water and the mixture was stirred at 80 ◦C for 1 h. Then appropriate amount of sodium tungstate dihydrate for above weight percent were added to solution. After then the mixture was stirred at 80 ◦C for 9 h and 82 ml of HCl solution was added drop wisely and mixed for 3 h at 80 ◦C. The precipitate was separated from mixture after 3 h at room temperature and then poured into petri dish and placed in convection oven overnight at 100 ◦C. afterward the powder was ground to fine particles and dried at 130 ◦C for 6 h in oven.

RESULTS AND DISCUSSION

SEM micrographs and Dispersive X-RAY analysis (EDAX)

Figure 1a shows SEM micrograph of well spherically distributed TiO_2 nanoparticles prepared by the second method in this work. Particle size estimated through this image was lower than 50 nm. Figure 1b represents SEM images of TiO_2 nanoparticles loaded with 20 w% of PW nanoparticles. Interesting point taken from these images was the particle size diminution in incorporated nanostructures by increasing PW amounts and remaining spherical morphology in both the cases. The X-ray dispersive analysis (EDX) of the samples prepared in the second method shown in Table 1, confirms appropriate percentage values of P and W incorporated in TiO_2 nanostructures.

Table 1. EDX ZAF quantification (standardless) elements of nanocomposites prepared in second synthesis method

Sample	%P	%W	%O	%Ti	%Au
10%wt.-nHPW/n-TiO_2	0.86	6.31	41.5	40.39	10.94
20%wt.-nHPW/n-TiO_2	1.29	8.46	36.31	40.0	14.31

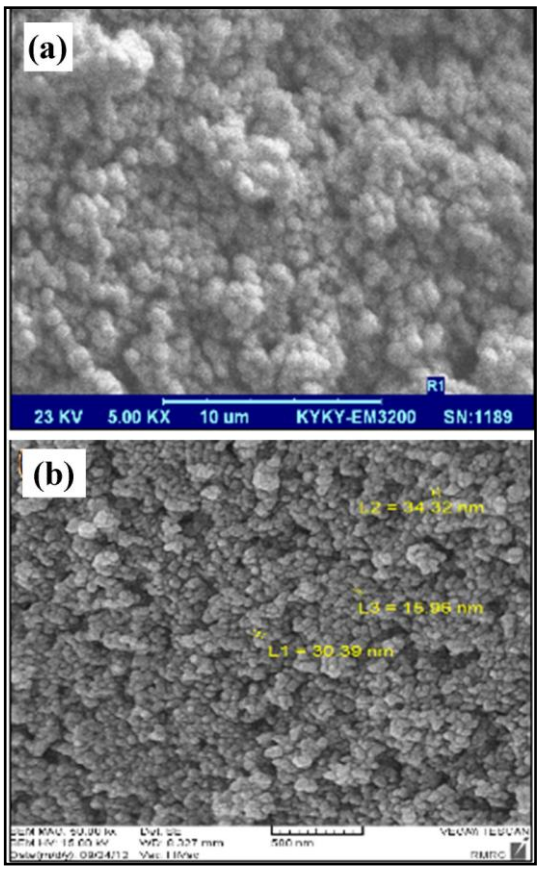

Fig. 1. a) TiO_2 nanoparticles; b) TiO_2 nanoparticles loaded by 20 % wt. of PW in second method (SA)

X-ray diffraction

Figure 2 displays XRD diffraction pattern of TiO_2 nanoparticles synthesized in this work. It consists of a mixture of anatase and rutile phases. The peaks appeared at 2θ= 25, 38.0, 48.0 and 54.3° elucidate the diffractions of the (101), (004), (200) corresponding to the anatase TiO2 phase (JCPDS no. 21-1272). The other additional peaks observed with a low intensities at (110) and (200) reflections, can be indexed to hexagonal lattice crystallinities of TiO_2 rutile phase (JCPDS no 77-0441) [16]. The average crystalline size from the most intense anatase peak was estimated to be 50 nm using Scherrer's formula:

$D=0.9\lambda/\beta\cos\theta$

Where 'λ' is wave length of X-Ray (0.1541 nm), 'β' is FWHM (full width at half maximum), 'θ' is diffraction angle and 'D' is particle diameter size.

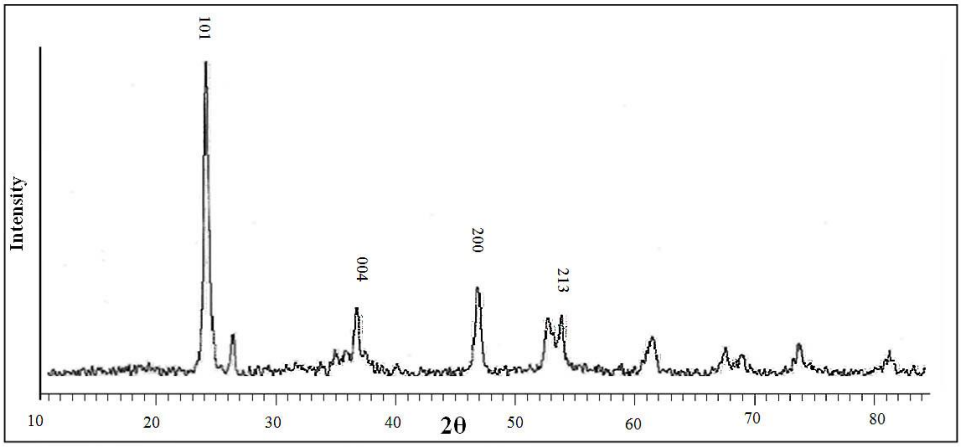

Fig. 2. XRD powder diffraction pattern of prepared nano TiO_2

Figure 3 Shows XRD powder diffraction pattern obtained for synthesized HPW with the characteristic peaks of polyoxotungstate having Keggin structure [17]. The peaks appeared in this figure corresponded to the plane (101), (004), (200) and (213) are in conformity with the formation of crystalline Keggin structure in the synthesized samples (JCPDS file No. 50-0305). The average crystalline size calculated from Scherrer's formula using the most intense peak was estimated to be around 18 nm.

Figure $4_{(A,B,C)}$ represent powder X-ray diffraction patterns of HPW, $n$$TiO_2$ in comparison with HPW/TiO_2 nanostructures incorporated with 10% wt. and 20 wt. % of HPW prepared in the first, second and third method. All X-ray diffraction patterns showed characteristic peaks of titania with additional peaks of HPW in a very low intensities showing formation of inorganic-inorganic composites or the presence of well dispersed of very small size of Keggin in or on the titania surface. The average particle size of as prepared nanocomposites prepared in the first, second and third method determined according to the Scherrer equation, are listed in Table 2. These data clearly indicated formation of core-shell nanostructured HPW/TiO_2 in all the cases.

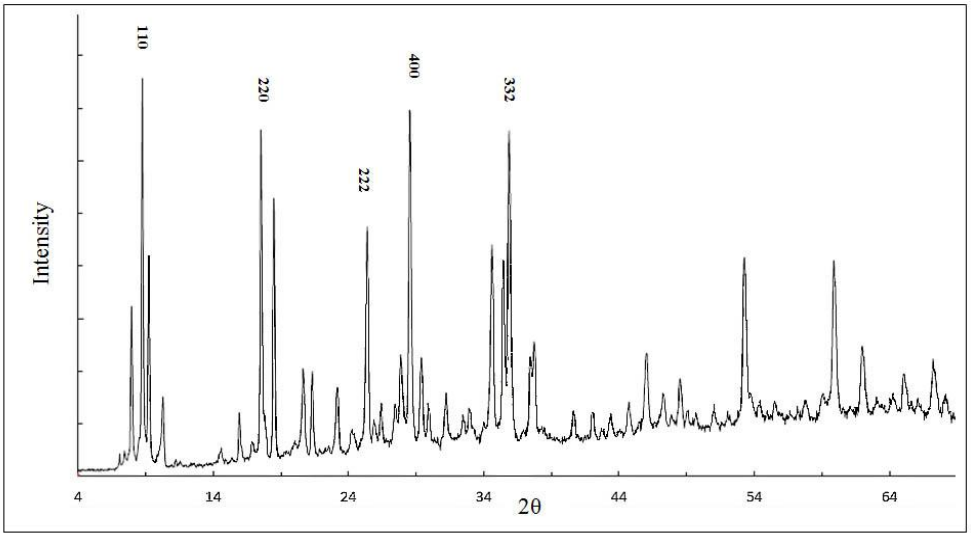

Fig. 3. XRD Pattern of nano HPW

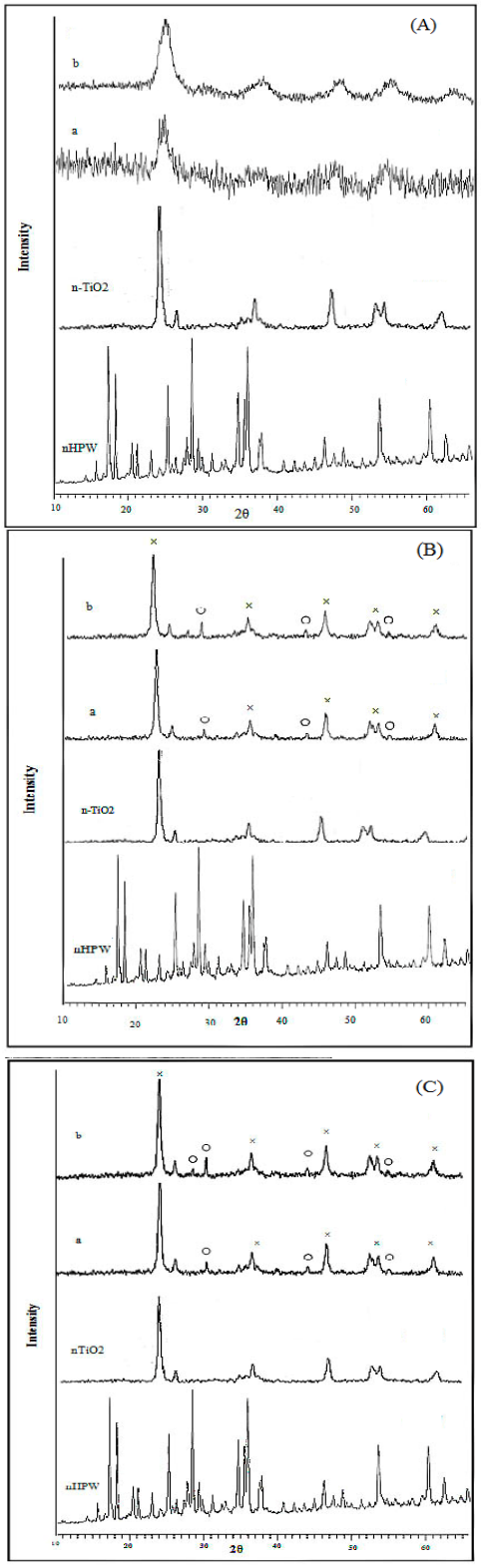

Fig. 4. (A,B,C). XRD powder diffraction patterns of $nTiO_2$ incorporated with: a) 10% wt.nHPW; b) 20% wt. of nHPW prepared in first (A), second (B) and third method (C).

i. Titania peaks are shown by ×
ii. HPW peaks are shown by ○

Table 2. Crystalline size of synthesized nanocomposites

Sample	Crystallite Size(nm)
Nano TiO_2	50
Nano HPW	18
10%wt.-nHPW/n-TiO_2 (a)	5.0
20%wt.-nHPW/n-TiO_2 (a)	10
10%wt.-nHPW/n-TiO_2 (b)	14
20%wt.-nHPW/n-TiO_2(b)	15
10%wt.-nHPW/n-TiO_2 (c)	15
20%wt.-nHPW/n-TiO_2(c)	16

FTIR Spectra

Figures 5(left, right) show FTIR spectra of nHPW/nTiO_2 samples prepared through the above mentioned methods with 10%wt. and 20 %wt. of HPW. In these Figures, infrared spectrum of the prepared HPW is included for comparative purposes. It has been widely reported that HPW with Keggin structures gives several strong typical IR bands assigned to HPW as follow: 1080 cm^{-1} (stretching frequency of P–O in the central PO_4 tetrahedron), 987 cm^{-1} (terminal bands for W O in the exterior WO_6 octahedron), 888 cm^{-1} and 805 cm^{-1} (bands for the W–O_b–W and W–O_c–W bridge and corner respectively) [18]. The FTIR results obtained for TiO_2 and TiO_2 supported nHPW samples with 10 and 20% wt HPW (Figures 5 L, R) showed typical bands for anatase phase at 700 cm^{-1} which is in good accordance with reported data and the peaks appeared in the range from 1100 cm^{-1} to 700 cm^{-1} can be ascribed to the stretch vibrations of P–O, W- O, and W–O–W bonds of the Keggin units respectively, indicating that the primary Keggin structures of these polyoxotungstates remain intact. *Distinct shifting* characteristic peaks of HPW incorporated nanostructures different percent of nPW on TiO_2, (10%wt. n-HPW/nTiO_2) to a higher frequency (Figure 5), shows occurrence and formation of new chemical linkage between terminal W- O, and W–O–W bonds with loaded TiO_2 component. Interesting point is that, remaining of the peak corresponding to the stretching frequency of P–O in the central PO4 tetrahedron and the peak at 987 cm^{-1} (terminal

bands for WO in the exterior WO6 octahedron) without any frequency shifting due to the linkage in TiO_2 supported HPW (Figure 5 right). This result in accordance with other published data can be due to the protection of WO_6 octahedron Keggin structure in TiO_2 supported HPW [19].

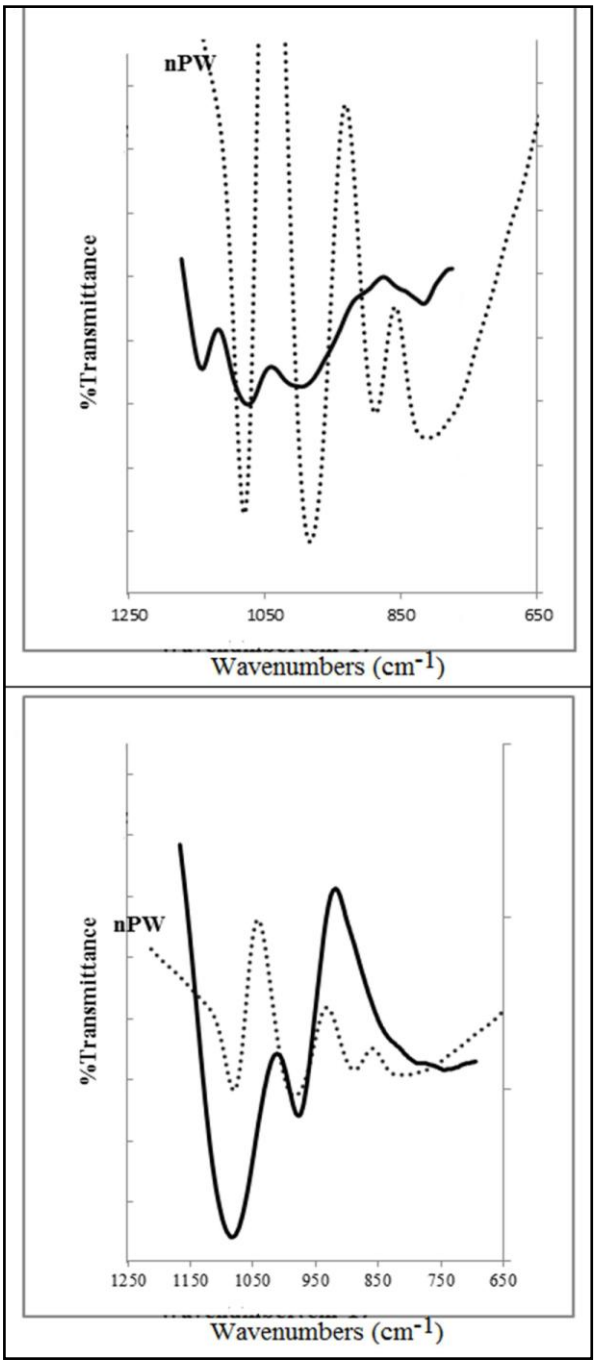

Fig. 5. FTIR Spectra of: Left) 10% nPW/TiO_2 ; right) 20% nPW/TiO_2
i. FTIR of PW showed as dashed line

CONCLUSIONS

We successfully prepared core shell HPW/TiO_2 nanostructure with various content of HPW (10 and 20 wt. %), by in situ sol-gel method. The X-ray diffraction patterns showed characteristic peaks of titania with additional peaks of HPW in a very low intensities. This may be due to the well dispersed small amount of Keggin structure on the titania surface without any structural changes. The SEM and EDX analysis data revealed presence of HPW incorporated with TiO_2 nanoparticles in all the prepared samples. The FTIR inspections confirmed interaction between HPW and TiO_2 with remaining HPW structure unchanged.

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REFERENCES

[1] Pope. M.T., Muller. A. (1991). Polyoxometalate Chemistry: An Old Field with New Dimensions in Several Disciplines. *Angew. Chem. Int. Ed. Engl*,. 30, 34-39.

[2] Katsoulis. D.E.(1998). A Survey of Applications of Polyoxometalates., *Chem. Rev*. 98, 359-365.

[3] Yamase. T.(1998). Photo- and electrochromism of polyoxometalates and related materials. *Chem. Rev*. 98, 307-315.

[4] Klmperer.W.E., G.G. Wall .(1998). Polyoxoanion Chemistry Moves toward the Future: From Solids and Solutions to Surfaces. *Chem. Rev*., 98, 297-311.

[5] Misono. M. (1987). Heterogeneus catalysis by heteropoly compounds of molybdenium

and tungsten., *Catal. Rev.-Sci. Eng.*, 29, 269-275.

[6] Rafiee. E., Rashidzadeh.S., Azad.A., (2007). Silica-supported heteropoly acids: Highly efficient catalysts for synthesis of α-aminonitriles, using trimethylsilyl cyanide or potassium cyanide. *J. Mol. Catal. A., 261 49–52*.

[7] Mizuno N, Misono. (1998). Heterogeneous catalysis. *Chem Rev.*, 98,199–218.

[8] (a) Molinari. A., Amadelli. R., Andreotti. L., Maldotti. A. (1999). Heterogenous catalysis for synthesis perposes: Oxygenation of Cyclohegzane with H3PW12O40 an (Nbu4O)4W10O32 Supported on silica. *J. Chem. Soc., Dalton Trans.*, 1203-1204; (b) Maldotti. A., Molinari. A., Varani. G., Lenarda. M., Storaro. L., Bigi. F., Maggi. R., Mazzacani. A., Sartori. G. .(2002). Immobilization of $(n\text{-}Bu_4N)4W_{10}O_{32}$ on mesoporous MCM-41 and amorphous silicas for photocatalytic oxidation of cycloalkanes with molecular oxygen. *J. Catal.*, 209, 210; Maldotti. A., Amadelli. R., Vital. I.,Borgatti. L., Molinari. A. (2003). CH_2Cl_2-assited functionalization of cycloalkenes by photoexcited $(nBu_4N)_4W_{10}O_{32}$ heterogenized on SiO_2., *J. Mol. Catal. A: Chem.*, 204–205, 703-704;(d) Molinari. A., Varani. G., Polo. E., Vaccari. S., Maldotti . A.(2007). Photocatalytic and catalytic activity of heterogenized W10O324- in the bromide assisted bromination of arenes and alkenes in the presence of oxygen. *J. Mol. Catal. A: Chem.*, 262,156; (e) Maldotti. A., Molinari. A., Bigi. F. (2008*).* Selective photooxidation of diols with silica bound W10O324-. *J. Catal*., 253,312-316.

[9] Guo. Y., Li. D., Hu. C., Wang. E., Wang. Y., Zhou. Y., Feng. S. (2001). Photocatalytic Degradation of Aqueous Organocholorine Pesticide on the Layered Double Hydroxide Pillared by Paratungstate A ion, $Mg_{12}Al_6(OH)_{36}(W_7O_{24})\bullet 4H_2O$., *Appl. Catal. B: Environ.*, 30,337-349.

[10] Ozer. R.R., Ferry. J.L. (2002*).* Photocatalytic Oxidation of Aqueous 1,2-Dichlorobenzene by Polyoxometalates Supported on the NaY Zeolite. *J. Phys. Chem. B.*, 106 ,4336-4339.

[11] Anandan. S., Ryu. S.Y., Cho. W., Yoon . M.(2003). Heteropolytungstic acid $(H_3PW_{12}O_{40})$—encapsulated into the titanium-exchanged HY (TiHY) zeolite: a novel photocatalyst for photoreduction of methyl orange. *J. Mol. Catal. A: Chem.*, 195, 201-208.

[12] Jiang. C., Guo. Y., Hu. C., C. Wang, D. Li .(2004). Photocatalytic degradation of dye naphthol blue black in the presence of zirconia-supported Ti-substituted Keggin-type polyoxometalates. *Mater. Res. Bull,. 39*, 251-261.

[13] Yang. Y., Wu. Q., Guo. Y., Hu, C. Wang E., (2005). Efficient degradation of dye pollutants on nanoporous polyoxotungstate–anatase composite under visible-light irradiation *J. Mol. Catal. A: Chem.*, 225, 203-212.

[14] Shen H.-Y., Mao H.-L., Ying L.-Y., Xia Q.-H. (2007). Photocatalytic selective aerobic oxidation of alcohols to aldehydes and ketones by HPW/MCM-41 in ionic liquids. *J. Mol. Catal. A: Chem*., 276, 73-79.

[15] Colmenares Juan Carlos, Aramendia Maria A., Marinas Alberto, Jose M. Marinas, Francisco J. Urbano .(2010). Titania nano-photocatalysts synthesized by ultrasound and microwave methodologies: Application in depuration of water from 3-chloropyridine. *J. Mol. Catal. A: Chem.*, 331, 58–63

[16] Tsakiridis. P.E., Oustadakis. P., Katsiapi. A., Perraki. M., Agatzini-Leonardou , S. (2011). Synthesis of TiO_2 nano-powders prepared from purified sulphate leach liquor of red mud. *J. Haza. Mat.*, 194, 42–47.

[17] Rafiee. E., Paknezhad. F., Shahebrahimi. Sh., Joshaghani. M., Eavani. S., Rashidzadeh. S. (2008). Acid catalysis of different supported heteropoly acids for a one-pot synthesis of β-acetamido ketones. *J. Mol. Catal. A: Chem* , .282, 92–98.

[18] Han Zhiyue, Zhang Jingchang, Yang Xiuying, Zhu Hong, Cao Weiliang. (2010). Synthesis and photoelectric property of poly (3-octylthiophene)/ titanium dioxide nano-composite material. *J.Mater Sci: Mater Electron* 21:554–561.

[19] Rafiee. E., Mahdavi. H., Eavani. S., Joshaghani. M., Shiri. F., (2009), Catalytic activity of tungstophosphoric acid supported on carriers of diverse acidity in the synthesis of enaminones, Applied Catalysis A: General 352, 202–207.

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