



# Acidic and neutral caesium salts of 12-molybdophosphoric acid supported on SBA-15 mesoporous silica. The influence of Cs concentration and surface coverage on textural and structural properties

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## ABSTRACT

The Cs salts of molybdophosphoric acid  $\text{Cs}_1\text{H}_2\text{PMo}_{12}\text{O}_{40}$  ( $\text{Cs}_1\text{PM}$ ) and  $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$  ( $\text{Cs}_3\text{PM}$ ), were supported on SBA-15 in the concentration of 20, 30 and 40 wt.% loadings. Because Cs salts are insoluble, the SBA-15 supported Cs-acid salts were prepared by two-step sequential impregnation and in situ reaction on the support. The structure and texture of these CsPM/SBA-15 composites were studied by XRD, SEM-EDS, FT-IR and micro-Raman spectroscopy, UV-vis-DRS and  $\text{N}_2$  adsorption. Thermal stability was investigated by thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The acidity of composites was studied by the adsorption of ammonia and its temperature programmed desorption – TPD using thermogravimetry. The evolved gases during the adsorption–desorption of ammonia on CsPM/SBA-15 composites were identified by online mass spectrometry coupled with thermal gravimetry technique. FT-IR and Raman studies demonstrated that CsPM maintained its Keggin structure after deposition on mesoporous SBA-15, regardless of the active phase concentration. For both  $\text{Cs}_1\text{H}_2\text{PMo}_{12}\text{O}_{40}$  and  $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ -SBA-15 composites could be observed an important increase of band gap energy in comparison with pure salts. The values of specific surface area of pure CsPM were increased by deposition on mesoporous silica support. The immobilization of CsPM on mesoporous SBA-15 obviously increases the thermal stability and the total acidity of the strong acidic sites of the Keggin structures in comparison with their parent bulk Cs salts.

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## 1. Introduction

Among the variety of catalytic systems, heteropolyacids (HPAs) with Keggin structure unsupported and supported on different materials have received much interest in the area of acid and oxidation catalysis due to their acidic and redox properties, which can be controlled at molecular level [1–5].

HPAs and particularly heteropolymolybdates are used as oxidation catalysts due to the relatively high oxidation ability of molybdenum ions. However, these HPAs are also associated with some limitations such as low surface area, relatively low thermal stability and high solubility in water and polar solvents. In order to

enhance these properties HPAs are usually impregnated on different porous materials with high surface area (hexagonal mesoporous silica, titania, carbon, zirconia, polymers, molecular sieves) [6–10].

During the last decades HPAs supported on mesoporous siliceous materials MCM-41 and SBA-15 have attracted much attention due to their very high surface area coupled with regular hexagonal array of uniform pore sizes within the mesoporous region. SBA-15 is a suitable support for acid catalysts as compared with MCM-41 possesses thicker pore walls, larger pore sizes and higher thermal and hydrothermal stability.

It is known that HPAs are strong and useful solid acids, but the amount of acidic sites on their surface is small because of their low surface area. Therefore, increasing the amount of surface acidic sites is an important task for the development of useful solid acids applied in different catalyzed reactions. Different attempts have

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been made to improve the efficiency of the HPAs by their supporting on various high surface area matrices and by replacement of protons with alkali metals [11–18].

Very few references have been reported concerning  $H_3[PMo_{12}O_{40}]$  and  $H_4[PMo_{11}VO_{40}]$  supported on mesoporous materials, majority of the studies have been focused on investigation of the most acidic HPA in the series, namely  $H_3PW_{12}O_{40}$  (HPW) [19–26].

Yang et al. [22] have studied HPW immobilized into SBA-15 by sol–gel technique. The hydrothermal stability of composites which was studied by washing the samples with an EtOH/H<sub>2</sub>O mixture increased in comparison with parent HPW. The sol–gel derived composite is more stable in the acidic property and the structural regularity of the mesoporous material than the impregnated sample. Palcheva et al. [6] have studied the effect of nickel salt of 12-tungstophosphoric acid,  $Ni_{3/2}PW_{12}O_{40}$ , as oxide precursors and of hetero-atoms modifying SBA-15 on the activity of NiW/(Al-, Ti-, W-) SBA-15 catalysts in thiophene hydrodesulphurization reaction. The NiW catalyst supported on W-containing SBA-15 showed higher performance in the HDS of thiophene as compared to the SBA-15 modified with Al and Ti. A series of Mo (W) catalysts promoted by Ni and supported on SBA-15 were prepared using Keggin-type heteropolyacids as active phase precursors. It was found that both Mo and W catalysts prepared from heteropolyacids showed better performance in hydrodesulphurization of 4,6-dimethyldibenzothiophene than the counterparts prepared from traditionally used Mo (W) ammonium salts [24]. HPM was successfully encapsulated into the super cage of Y zeolite promoted by Cs counter cation in zeolite matrix, using 2.5% aqueous solution of  $Cs_2CO_3$ . The 30% HPM-CsY catalyst exhibits considerable catalytic activity in liquid phase esterification of acetic acid with n-butanol under the optimal reaction conditions [26].

By substitution of H<sup>+</sup> protons with alkali cations, important modifications take place on the surface area, pore structure, solubility and hydrophobicity, in comparison to the parent HPA. HPAs salts with large monovalent ions, such as  $NH_4^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Ag^+$  and  $Tl^+$ , are practically insoluble in water or other polar solvents and possess high surface areas [27]. The higher surface area, mainly arising from microporosity observed for caesium salts with Cs/W ratio of >2 compensates the loss of acidic protons. It is supposed that in salts with number of counter ions (which replaces hydrogen ions)  $x < 2$ , acidic salt is a heterogeneous mixture of microporous neutral salt and unreacted acid; in salts with  $x > 2$  the salts are composed of grains with crystalline core of neutral salt covered by surface layer of unreacted acid [28–31].

Partial substitution of protons by these cations may result in changes of the number of available surface acidic sites. For example, the salt  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  was reported as superior catalyst which exhibit significantly higher activity than the parent acid in gas phase acid-catalyzed reactions [32]. However, the caesium salt of HPA forms colloidal suspension in polar media causing filtration problems. This drawback could be overcome by stabilizing Cs salt of HPA in a porous support.

A major disadvantage of HPAs salts with big cations consists in their insolubility which makes impossible the conventional aqueous impregnation on different supports. In order to overcome this disadvantage, a sequential impregnation was used and in situ reaction on two types of supports: silica and  $\gamma-Al_2O_3$  [11].  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  heteropolyacid salt prepared by the same technique by deposition of the parent salt on SBA-15 support was studied by Rao et al. As Cs acid salts are insoluble, the SBA-15 supported Cs-acid salt was prepared by two-step sequential impregnation and in situ reaction on the support [16]. Silica supported ammonium salt of 12-molybdophosphoric acid catalysts has been investigated by Gong et al. on liquid nitration of

benzene with 65% nitric acid as nitrating agent [33]. These catalysts with different loadings were prepared by sol–gel method and supported catalysts had high nitration reaction catalytic activity and selectivity over nitrobenzene.

In the past decades different HPAs salts (especially of HPW acid) based on only one type of cation or mixed salts have been extensively reported, but the influence of cation concentration and of the surface coverage of Cs salts of 12-molybdophosphoric supported on SBA-15 in reference to the bulk solid HPM have not been significantly studied in the literature.

In this study was carried out the preparation of the Cs salts of molybdophosphoric acid  $Cs_1H_2PMo_{12}O_{40}$  (Cs<sub>1</sub>PM), and  $Cs_3PMo_{12}O_{40}$  (Cs<sub>3</sub>PM), by supporting on SBA-15 molecular sieve, in the concentration of 20, 30 and 40 wt.% loading. The goal of this work was to characterize the texture, structure and the influence of Cs concentration and surface coverage of these heteropolyacids salts in reference to the bulk solid heteropolyacids. The amount and strength of the acidic sites were calculated by desorption of ammonia, measured by thermal analysis. For the clarity of discussion, some data obtained for  $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$  samples presented in our previous paper [34] are also given.

## 2. Experimental

### 2.1. Samples preparation

The bulk CsPM with Cs/Keggin unit (KU) ratio of 1 and 3 were prepared by adding slowly drop wise the required amount of aqueous caesium nitrate  $CsNO_3$  to aqueous  $H_3PMo_{12}O_{40}$  with vigorous stirring at room temperature. The precipitates obtained were aged in parent solution for 24 h at room temperature, followed by evaporation in vacuum at 50 °C, and finally calcination at 300 °C for 4 h.

The CsPM/SBA-15 composites were synthesized as follows: first caesium nitrate was impregnated by aqueous incipient wetness onto SBA-15 molecular sieve, dried and calcined at 300 °C and finally 12-molybdophosphoric acid was impregnated by a similar aqueous impregnation route. The detailed preparation procedure was given in our previous paper [34].

Two types of Cs salts of molybdophosphoric acid ( $Cs_1H_2PMo_{12}O_{40}$  (Cs<sub>1</sub>PM), and  $Cs_3PMo_{12}O_{40}$  (Cs<sub>3</sub>PM)), were deposited in the concentration of 20, 30 and 40 wt.% concentration loadings.

Mesoporous silica SBA-15 was synthesized according to the procedure developed by Zhao et al. by the hydrolysis of tetraethyl orthosilicate (TEOS) using a P123 block copolymer as surfactant [35,36].

The structure and texture of CsPM supported on SBA-15 were studied by XRD, FT-IR and micro-Raman spectroscopy, SEM-EDX and low temperature nitrogen adsorption technique. Thermal stability was studied by TG–DTA and DSC methods.

### 2.2. Measurements of textural properties

Textural characteristics of the outgassed samples were obtained from nitrogen physisorption using a Quantachrome instrument, Nova 2000 series. The specific surface area  $S_{BET}$ , average 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 250 °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.

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