



The influence of reagent used for the precipitation of Cs₂HPW₁₂O₄₀ salt on its textural and catalytic properties

L. Matachowski^{a,*}, A. Drelinkiewicz^a, E. Lalik^a, D. Mucha^a, B. Gil^b, Z. Brożek-Mucha^c, Z. Olejniczak^d

^a Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Kraków, Poland

^b Jagiellonian University, Department of Chemistry, ul. R. Ingardena 3, 30-060 Kraków, Poland

^c Institute of Forensic Research, ul. Westerplatte 9, 31-033 Kraków, Poland

^d Institute of Nuclear Physics Polish Academy of Sciences, ul. Radzikowskiego 152, Kraków, Poland

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ABSTRACT

The series of Cs₂HPW₁₂O₄₀ samples was prepared using various reagents, namely Cs₂CO₃ and CsCl, as the precipitating agent. Moreover, the modification of preparation procedure consisting of HCl addition to the colloidal solution of Cs₂HPW₁₂O₄₀ salt, precipitated previously with Cs₂CO₃ and H₃PW₁₂O₄₀, was also studied. The aim of present research was to recognize the role of precipitating agent in the physicochemical and catalytic properties of Cs₂HPW₁₂O₄₀ samples. The samples were characterized by number of techniques, BET, FT-IR, ³¹P NMR, XRD, XPS, TPD-MS, laser diffraction, NH₃ sorption. It was observed that the lattice parameters and the environment of phosphorous were the same in all studied samples. The Cs₂HPW₁₂O₄₀ salt prepared by Cs₂CO₃ exhibited very low specific surface area of about 1 m²/g. In contrast, the usage of CsCl yielded the sample of remarkably higher surface area (~78 m²/g) and dramatically higher catalytic activity for dehydration of ethanol. Thus, an effect of precipitating agent can be ascribed to its influence on the size of colloidal particles formed upon preparation procedure. It has been postulated that the adsorption of HCl/chloride ions on the surface of primary particles of Cs₂HPW₁₂O₄₀ salt facilitated the formation of mesoporous structure, which determined its sorption and catalytic properties.

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1. Introduction

The Keggin-type heteropolyacids are known to be effective catalysts in numerous reactions carried out under both homogeneous as well as heterogeneous conditions [1–3]. An arrangement of large anions, called the Keggin units, in their structures enables high mobility of protons within the lattice, which plays an important role in their catalytic activity. This activity is further improved by a partial substitution of protons with some sizeable cations like Cs⁺ without significant changes in the arrangement of Keggin units. The presence of large cations within such structures increases their porosity as well as sorption properties.

Among the existing Keggin-type heteropolyacids, the solid dodecatungstophosphoric acid has a high acidity combined with a good thermal stability. The two acidic cesium salts of H₃PW₁₂O₄₀ (HPW) that have attracted most researchers' attention are: Cs_{2.5}H_{0.5}PW₁₂O₄₀ and Cs₂HPW₁₂O₄₀. Both such salts have structure built of Keggin units, but they differ in the fraction of protons replaced by the cesium cations. Although the Cs_{2.5}H_{0.5}PW₁₂O₄₀ salt has less protons than the Cs₂HPW₁₂O₄₀ salt, its extended microporous structure resulting in relatively large surface area [4–8] have been well established to be the property

responsible for its high catalytic activity in number of reaction [9,10]. The case of Cs₂HPW₁₂O₄₀ salt is different because catalytic and sorption properties of this salt are to high extent determined by the method of the salt preparation.

The Cs₂HPW₁₂O₄₀ salt can be precipitated from an aqueous solution of H₃PW₁₂O₄₀ using different reagents, such as Cs₂CO₃, CsCl, or CsNO₃. Usage the cesium carbonate offers an advantage due to the formation of CO₂, which is easily removable from the reaction system upon drying of the salt precipitate. However, the application of Cs₂CO₃ as precipitating agent leads to extremely low specific surface area of the obtained Cs₂HPW₁₂O₄₀ salt. In number of studies Cs₂HPW₁₂O₄₀ samples with specific surface area (determined from nitrogen adsorption–desorption isotherms), which did not exceed 1 m²/g were reported [11–13]. For instance, Okuhara [1] reported the Cs₂HPW₁₂O₄₀ salt of surface area as low as 0.5 m²/g. On the other hand, the specific surface area of Cs₂HPW₁₂O₄₀ samples prepared from the cesium chloride or nitrate was reported to be distinctly higher, ranging from 43 [14] to 71 m²/g [15]. This essential difference in specific surface area may explain high catalytic activity of the latter samples in the *n*-butane isomerisation [15,16]. Similar effect concerning the influence of reagent on specific surface area of ammonium salt of tungstophosphoric acid was also observed by Lapham and Moffat [17]. The surface areas of samples prepared from ammonium nitrate, chloride, and carbonate were practically the same while surface

* Corresponding author. Tel.: +48 126395101; fax: +48 124251923.

E-mail address: ncmatach@cyf-kr.edu.pl (L. Matachowski).

area of the salt prepared from the ammonium sulfate was at least 2 times smaller. To the best of our knowledge, the reason of these differences has not been explained till now, although high surface area of catalysts is a crucial for their catalytic activities.

In the present work the samples of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt prepared using either Cs_2CO_3 and CsCl as the precipitating agents were studied. The modification of the $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt, obtained with cesium carbonate, involving the addition of HCl was also presented. The aim of this work was to elucidate a role of precipitating agent in the physicochemical and catalytic properties of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt. The characterization of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples by FT-IR, XRD, ^{31}P MAS NMR and TPD-MS techniques showed an essential difference in their physicochemical properties. In order to compare their catalytic reactivity, dehydration of ethanol was chosen. This reaction is often employed as a test reaction for acidic catalysts.

2. Experimental

2.1. Catalysts preparation

The $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples were prepared using commercially available $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ (Merck), cesium carbonate (Aldrich) and cesium chloride (POCH) reagents. The $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salts were prepared by adding predetermined amounts of a 0.04 M aqueous solution of Cs_2CO_3 or CsCl to a 0.1 M solution of HPW at room temperature without stirring. The precipitates obtained together with the solution were subsequently slowly evaporated to dryness at 313 K. The samples prepared using Cs_2CO_3 or CsCl were denoted as $\text{Cs}_2(\text{carbonate})$ and $\text{Cs}_2(\text{chloride})$, respectively. The $\text{Cs}_2(\text{carbonate}/\text{HCl})$ samples were prepared by the addition of HCl solution (0.1 M) to the pre-formed $\text{Cs}_2(\text{carbonate})$ colloidal solution at ambient temperature without stirring. Three samples were prepared using the amounts of HCl solution corresponding to quarter or half or total of the HCl amount existing in the solution upon the $\text{Cs}_2(\text{chloride})$ precipitation. Then, the sample in solution was subjected to slow evaporation at 313 K, similarly as described before.

2.2. Catalysts characterization

The specific surface areas of the $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples were determined using the BET method. Prior to the measurements, the samples were heated and degassed under vacuum at 473 K for 2 h. The adsorption–desorption isotherms for nitrogen were obtained at 77 K using an Autosorb-1 (Quantachrome). The surface area and the pore distribution were calculated by BET and BJH desorption isotherms. The isotherms for water vapor were obtained at 297 K with Hydrosorb 1000 (Quantachrome).

The FT-IR spectra were recorded on the Bruker IFS 48 spectrometer equipped with a MCT detector, in the absorption mode, with a spectral resolution of 2 cm^{-1} . An IR environmental cell with ZnSe windows was used for the measurements of NH_3 sorption performed ‘in situ’. The samples of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ were suspended in water, and the slurry was placed on a silicon wafer and left to evaporate. Then, the wafer was placed in the IR cell and slowly heated (ca. 1 h) under evacuation (ca. 0.13 Pa) up to temperature of 473 K. After the activation, the sample was cooled down to 253 K and the IR spectrum was registered. Then, ammonia gas (Linde Gas, 3.5) was dosed progressively to the activated sample and after each dose the spectrum was recorded.

Solid State Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectra were measured with the home-made pulse-NMR spectrometer at the magnetic field of 7.05 T. A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to record the MAS spectra at 4 kHz spinning speed. The ^{31}P MAS NMR spectra were measured at 121.3 MHz,

using a single $2\text{ }\mu\text{s}$ rf pulse, corresponding to $\pi/2$ flipping angle. The acquisition delay used in accumulation was 60 s, and the number of acquisitions was equal to 64. The frequency scale in ppm was referenced to the ^{31}P resonance in the liquid sample of H_3PO_4 as 0 ppm.

The X-ray diffraction patterns obtained at ambient temperature were recorded in the range of $2\theta = 8\text{--}70^\circ$, step size 0.02° and 12 s/step using the Siemens D5005 diffractometer ($\text{CuK}\alpha$ radiation, 40 kV, 40 mA) equipped with the secondary beam graphite monochromator. In order to remove the crystallization water, before measurements, the samples were heated at 363 K. Full-matrix Rietveld refinement, performed by commercial program TOPAS, was applied to calculate lattice parameters and crystallite sizes of cesium samples [18,19]. As a starting model, $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ (space group $Pn\bar{3}m$ (2 2 4)) modified by replacing the H_5O_2^+ by the cesium cations in $[\frac{1}{4}, \frac{1}{4}, \frac{3}{4}]$ position, was used. It was according to Brown et al. [20] who postulated that each cesium cation must replace one H_5O_2^+ ion. All crystal planes are taken into account in the Rietveld refinement because in this ‘‘ab initio’’ method the diffractogram is fitted using the structure of the phase. The crystallite sizes were calculated using the $L_{\text{Vol}}\text{-IB}$ method, which is based on the widening of the reflection fitted by pseudo-Voigt V curve. In order to determine the content of crystalline and amorphous phases, the XRD measurements with the addition of 30–50% of silicon (p.a. 325 mesh, Aldrich) were carried out. The content of amorphous phase was calculated using the method described previously [21]. The XRD measurements were also performed at 573 K under air atmosphere using additionally XRK900 (Anton Paar) reaction chamber. The pattern at 573 K was collected in the range of $2\theta = 20\text{--}80^\circ$, step size 0.04° and 2 s/step.

The TPD-MS measurements were performed within the temperature range 313–773 K (15 K/min heating rate) using home-made apparatus with the mass spectrometry analysis of desorbed gases. The helium was used as the carrier gas with flow rate of $2\text{ cm}^3/\text{min}$.

The size distribution of particles in the colloidal solution after the precipitation of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples was analyzed using Laser Diffraction Particle Size Analyzer LS 13 320 (Beckman Coulter Inc.). The size of particles was measured in the range of 40 nm–2 μm .

The microcalorimetric measurements of ammonia sorption were carried out at 293 K using MICROSCAL gas flow-through microcalorimeter [22]. Prior to the experiments the samples were heated ‘in situ’ at 473 K for 2 h in the flow of helium. After cooling down and equilibrating system at 293 K, ammonia was sorbed from the helium carrier gas containing 1% of NH_3 flowing through the cell at $1\text{ cm}^3/\text{min}$ under normal pressure. Concurrently with the heat evolution, the uptake of ammonia from the carrier gas was measured using thermoconductivity detector (downstream detector, DSD).

2.3. Catalytic tests

The dehydration of ethanol was studied as a test catalytic reaction. The catalytic experiments were carried out using a quartz flow-through microreactor with the concentration of ethanol in the nitrogen of $1.5\text{ mol}/\text{dcm}^3$, at the temperature ranging from 398 to 523 K and $\text{GHSV} = 10000\text{ h}^{-1}$. Prior to the catalytic tests, the samples were standardized under flowing of nitrogen at 523 K for 4 h. The concentrations of ethanol, ethylene and diethyl ether were analyzed using SRI 8610B gas chromatograph equipped with HayeSep D column and TCD and FID detectors.

3. Results and discussion

The pH of the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution during precipitation of its cesium salt is a fundamental factor influencing the formation of various heteropolyacid structures, other than the Keggin structure,

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