

Proton enriched high-surface-area cesium salt of phosphotungstic heteropolyacid with enhanced catalytic activity fabricated by nanocasting strategy

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Abstract

The elimination by HF of the silica matrix from the composites obtained by the two-step reaction deposition of $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ (CsHPW) salt nanocrystals with a Cs/W₁₂ ratio equal 2.5 on SBA-15 yields materials with substantially lower Cs/W₁₂ ratios of 1.7–2.0. The value of the Cs/W₁₂ ratio in the nanocasts is determined by the Cs-precursor (Cs *n*-propoxide or Cs-acetate) used at the first stage of materials preparation. The surface area of the CsHPW nanocasts is 41–45 times higher than their co-precipitated analogs at the same Cs/W₁₂ ratios. We report here that implementation of the nanocasting preparation technique yields for the first time a bulk CsHPW material that combines a high concentration of acid sites (Cs/W₁₂ = 1.7–2.0) with a high surface area of 41–93 m² g^{−1}. Co-precipitated analogues at the same Cs/W₁₂ ratios are nonporous and exhibit a surface area smaller than 5 m² g^{−1}. Our nanocasted CsHPW materials are stable against leaching and colloidalization in polar solvents, and their catalytic performance exceeded that of bulk $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, known as the most active among the acidic HPW salts. The catalytic activity of CsHPW nanocasts in MTBE synthesis and in the isopropanol dehydration reactions is shown to be higher by a factor of 2–3 than that of the standard $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ material.

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1. Introduction

Dodecatungstophosphoric acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (hereafter HPW) is the strongest acid among the heteropolyacids that has been employed as catalysts in reactions of hydrocarbons, such as acylation, alkylation, esterification, isomerization, etc. [1,2]. Its low surface area (<5 m² g^{−1}), limiting the accessibility to its acid sites, and its high affinity to polar solvents, making it soluble, called for suitable modification of the bulk acid. The two approaches that have addressed these two characteristics and their consequences are the dispersion and chemical fixation of the acid on an oxide support [3,4] and the conversion of the acid into a corresponding alkali metal salts, yielding an acidic material insoluble even in polar solvents [5]. The loss of

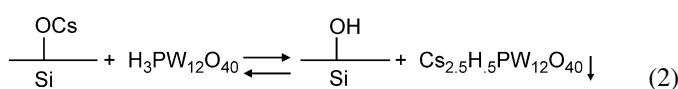
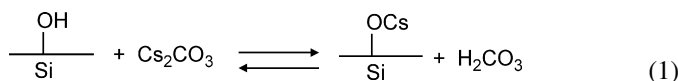
acidic protons in the alkali metal salts is compensated by an accompanied increase in microporosity. This has been observed for cesium salts exhibiting a Cs/W₁₂ ratio larger than 2 [6,7]. This microporosity increases the accessibility of reacting molecules to acid sites in these Cs-salts as compared to salts with Cs/W₁₂ ratios smaller than 2 that are nonporous and have surface area smaller than 3 m² g^{−1} [2,5]. The CsHPW salts with Cs/W₁₂ > 2 have been widely tested, and it was found that the composition $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ shows the highest catalytic activity [2,8].

The tendency of the cesium salts of HPW (hereafter CsHPW) to form milky suspensions in polar substrates, thus creating filtration problems in liquid phase reactions and a pressure drop in fixed bed reactors, limits their practical applications [9]. This drawback can be circumvented by stabilizing CsHPW in porous oxide matrices [10–19]. Besides fixation of CsHPW, preventing its colloidalization in polar solutions, the main research effort in these materials has been to increase the catalytic activity of the

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salt with the optimal composition by increasing the dispersion of its crystals.

Soled et al. [10] proposed an original solution that was intended to solve two practical difficulties: the insertion of insoluble CsHPW salt inside the pores of silica-gel and the appearance of fine dispersions of Keggin units that partially exchange with Cs^+ -ions at the supports surface. They accomplished this by a “reaction deposition” technique consisting of two steps: first grafting of Cs^+ -ions onto the silica surface (1) followed by an exchange of these surface Cs^+ -ions with protons of the HPW molecules dissolved in water (2). This resulted in a deposition of insoluble Cs-salt inside the pores of the silica.



A problem with this procedure has been the precipitation of CsHPW salt on the outer spheres and at the external surfaces of the silica-gel pellets during step (2). Later Wang et al. [13,14] suggested that the Cs^+ cations that are grafted during step (1) are re-dissolved in the acidic aqueous solution of HPW via hydrolysis of the Si–O–Cs moieties at step (2). This enables the migration of Cs^+ cations to the outer surface of the silica particles, causing a lowering of the dispersion of the supported CsHPW. The improved reaction deposition technique using HPW solutions in non-aqueous solvents, especially in alcohols that does not hydrolyze the O–Cs bonds, yielded a uniform distribution of CsHPW salt in MCM-41 crystals versus segregated CsHPW/MCM-41 and CsHPW phases obtained from aqueous solution, as observed by TEM [13].

Implementation of this improved technique resulted in a series of CsHPW catalytic materials supported on silica-gel [11,12], on mesostructured silicas MCM-41 [12–15] and SBA-15 [16], on amine-modified silica [17] as well as on alumina-silicas K-10 clay [18] and zeolite USY [19] that demonstrated better catalytic performance compared with bulk salt. The deposition of CsHPW on silica using the optimized reaction deposition methods increased its specific activity by 2–10 times, calculated based on the weight of the catalytic phase and depending on the texture of the support, the loading and type of the catalytic reaction. Unfortunately, most of these effects are compensated by a dilution of the catalytic phase with the inert silica. As a result the activity of the supported catalysts does not exceed the activity of their bulk counterparts by more than 50%, when based on the total weight of the catalyst.

The real chemical composition of the CsHPW phase and its accessible surface inside supporting composite materials, determining the potential performance of the catalytic phase, remain unknown. It was shown that all the existing protons in bulk microporous CsHPW with a crystal size of 12 nm and a Cs/W₁₂ ratio of 2.5 are available for adsorption of NH_3 [6] and pyridine [20]. This makes it doubtful that a further increase of the acidity and catalytic activity can be expected for decreasing crystal sizes to less than 10 nm. Another source for a possible increase of the

catalytic reaction rates by diminishing the diffusion limitations of reagents/products should be ruled out, since the diffusion limitations in microporous materials like zeolites are insignificant in this range of crystal sizes [21].

Absorption measurements have demonstrated a more than 3-fold increase of the amount of adsorbed ammonia per gram of CsHPW phase after its insertion in SBA-15 at a nominal Cs/W₁₂ ratio of 2.5 [16]. The 2–10-fold increase of specific catalytic activities after deposition of CsHPW salts on silica observed by several groups is consistent with these data. One of possible explanations for these phenomena could be the formation and fixation of highly acidic nanocrystals of the CsHPW phase with Cs/W₁₂ < 2.5 inside the silica pores. The high catalytic activity of such proton enriched materials on silica supports, prepared at low nominal Cs/W₁₂ ratios, was observed previously [11,12]. The potential performance of these nanocrystals would be even higher if no blockage of part of them inside silica pores would occur.

In the present work we will show that indeed in a material supporting CsHPW and showing a nominal Cs/W₁₂ ratio equal to 2.5 the actual Cs/W₁₂ ratio of the CsHPW crystals, after the removal of the support, is substantially lower. The reason for this being that part of the Cs ions inserted at step (1) can be located in silica micropores and that during step (2) of the reaction deposition part of the Cs atoms are not accessible for the $\text{Cs}^+ \leftrightarrow \text{H}^+$ exchange reaction with the bulky Keggin anions, thus yielding a substantially lower actual Cs/W₁₂ ratio in supported nanocrystals than following from the nominal composition.

This was confirmed by implementation of nanocasting strategy [22] for preparation of CsHPW materials where they were first stabilized in the mesoporous matrix playing a role of a scaffold for catalytic phase and then liberated from the matrix forming a nanocast. In the next sections the materials at the different stages of the preparation of the CsHPW nanocasts by reaction deposition and matrix extraction using SBA-15 support as a scaffold are characterized with the help of HRTEM, HRSEM, EDX, N₂ adsorption, WAXS, NH_3 -TPD, XPS and MAS NMR. In addition the catalytic performance of the resulting nanocasts with Cs/W₁₂ ratios smaller than 2 and with high surface area of 41–93 m² g^{−1} are tested via several acid-catalyzed reactions.

2. Experimental

2.1. Preparation of the materials

Bulk CsHPW samples with a Cs/W₁₂ ratio between 1.5 and 2.5 were prepared from aqueous solutions of Cs_2CO_3 (Aldrich) and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Aldrich) by titration according to a previously reported procedure [5,23]. An appropriate amount of aqueous solution of Cs_2CO_3 (0.2 mol/l) was added dropwise to an aqueous solution of HPW (0.08 mol/l) at a rate of ~1 ml/min. The milky colloidal solution was stirred overnight and then evaporated at 318 K. The remaining solid was finally calcined in air at 573 K for 2 h.

SBA-15 employed in this study was prepared, following the procedure described elsewhere [24], via crystallization from

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