



Preparation and characterization of mesoporous $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt, active in transformation of m-xylene

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ABSTRACT

The samples of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt were precipitated with CsCl, CsBr or CsI reagent as well as with commonly used Cs_2CO_3 . The use of cesium halides resulted in the $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples of mesoporous structure composed of relatively loosely aggregated primary particles. It was observed that the type of halogen ion influenced textural properties of the $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples. As the atomic size of halogen ion increased (from Cl to I), the specific surface area and microporosity decreased. The so-obtained samples exhibited textural and morphological features similar to those of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ salt. In the transformation of m-xylene, the pore-size sensitive reaction, the catalytic activity of the $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples prepared with CsBr and CsI reagents was about two-fold higher than that of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ salt. All these samples exhibited similar strength of acid sites. Therefore, high catalytic activity of the samples prepared with CsBr and CsI could be ascribed to their open pore structure, which allowed the accessibility of almost all active sites for m-xylene molecules.

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1. Introduction

The cesium salts of 12-tungstophosphoric acid have been widely studied since over 30 years [1–5]. Among them $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salts have attracted most researchers' attention. They both have structures built of Keggin units, which differ in the fraction of protons replaced by the cesium cations. Till now, the studies were mostly devoted to the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ salt because of its outstanding activity in a number of acid centers catalyzed reactions [6,7]. This was a result of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ high specific surface area due to its micro- and mesoporous structure allowing highly effective utilization of protons. However, the stoichiometry of the $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt also could suggest its possible high activity in acid centers catalyzed reactions.

The $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt could be precipitated from an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ using different reagents, such as Cs_2CO_3 , CsCl or CsNO_3 . However, the application of Cs_2CO_3 as the precipitating agent yielded material of extremely low specific surface area. Several researchers reported, that such prepared $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt had specific surface area (determined from adsorption–desorption isotherm of nitrogen), which did not exceed $1 \text{ m}^2/\text{g}$ [8–10]. On

the other hand, the specific surface area of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ samples prepared using cesium chloride or nitrate was reported to be distinctly higher, ranging from $43 \text{ m}^2/\text{g}$ [11] to $72 \text{ m}^2/\text{g}$ [12]. This explained high catalytic activity of the latter samples in the n-butane isomerization [12,13]. Similar effect was observed in our recent studies [14]. Textural features of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt were improved, when instead of Cs_2CO_3 reactant, the CsCl was applied as precipitating agent. The so-obtained $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt had specific surface area of about $78 \text{ m}^2/\text{g}$ and partially mesoporous structure (average pore diameter of about 3.5 nm) [14]. Results presented recently [14] allowed us to postulate that the composition of supernatant solution upon $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ precipitation, played an essential role in the process of primary crystallites aggregation. It seemed to be very probable that Cl^-/HCl existing in colloidal solution strongly influenced this process. The adsorption of chloride ions on the surface of primary particles of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ salt, facilitated the formation of mesoporous structure [14]. The influence of the type of an anion (nitrate, chloride or carbonate) in the precipitating reagent on the specific surface area of ammonium salt of tungstophosphoric acid was also observed by Lapham and Moffat [15]. Furthermore, specific surface area, pore volume and pore width were observed to be cation-dependent (Cs^+ , K^+ , Rb^+) during precipitation of the $\text{M}_{2.1}\text{H}_{0.9}\text{PW}_{12}\text{O}_{40}$ salts by the appropriate carbonates [16]. Although, according to these authors this effect is very interesting from the viewpoint of porosity control

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