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

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**A B S T R A C T**

The samples of Cs$_2$HPW$_{12}$O$_{40}$ salt were precipitated with CsCl, CsBr or CsI reagent as well as with commonly used Cs$_2$CO$_3$. The use of cesium halides resulted in the Cs$_2$HPW$_{12}$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 Cs$_2$HPW$_{12}$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 Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ salt. In the transformation of m-xylene, the pore-sensitive reaction, the catalytic activity of the Cs$_2$HPW$_{12}$O$_{40}$ samples prepared with CsBr and CsI reagents was about two-fold higher than that of Cs$_{2.5}$H$_{0.5}$PW$_{12}$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 Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ and Cs$_2$HPW$_{12}$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 Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ salt because of its outstanding activity in a number of acid centers catalyzed reactions [6,7]. This was a result of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ high specific surface area due to its micro- and mesoporous structure allowing highly effective utilization of protons. However, the stoichiometry of the Cs$_2$HPW$_{12}$O$_{40}$ salt also could suggest its possible high activity in acid centers catalyzed reactions.

The Cs$_2$HPW$_{12}$O$_{40}$ salt could be precipitated from an aqueous solution of H$_3$PW$_{12}$O$_{40}$ using different reagents, such as Cs$_2$CO$_3$, CsCl or CsNO$_3$. However, the application of Cs$_2$CO$_3$ as the precipitating agent yielded material of extremely low specific surface area. Several researchers reported, that such prepared Cs$_2$HPW$_{12}$O$_{40}$ salt had specific surface area (determined from adsorption–desorption isotherm of nitrogen), which did not exceed 1 m$^2$/g [8–10]. On the other hand, the specific surface area of Cs$_2$HPW$_{12}$O$_{40}$ samples prepared using cesium chloride or nitrate was reported to be distinctly higher, ranging from 43 m$^2$/g [11] to 72 m$^2$/g [12]. This explained high catalytic activity of the latter samples in n-butane isomerization [12,13]. Similar effect was observed in our recent studies [14]. Textural features of Cs$_2$HPW$_{12}$O$_{40}$ salt were improved, when instead of Cs$_2$CO$_3$ reactant, the CsCl was applied as precipitating agent. The so-obtained Cs$_2$HPW$_{12}$O$_{40}$ salt had specific surface area of about 78 m$^2$/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 Cs$_2$HPW$_{12}$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 colloid solution strongly influenced this process. The adsorption of chloride ions on the surface of primary particles of Cs$_2$HPW$_{12}$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 M$_2$H$_{0.5}$PW$_{12}$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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