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Preparation and characterization of mesoporous Cs₂HPW₁₂O₄₀ salt, active in transformation of m-xylene



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ABSTRACT

The samples of $Cs_2HPW_{12}O_{40}$ 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 $Cs_2HPW_{12}O_{40}$ 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 $Cs_2HPW_{12}O_{40}$ 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-size sensitive reaction, the catalytic activity of the $Cs_2HPW_{12}O_{40}$ 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 $Cs_2HPW_{12}O_{40}$ 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 $Cs_2HPW_{12}O_{40}$ salt also could suggest its possible high activity in acid centers catalyzed reactions.

The Cs₂HPW₁₂O₄₀ salt could be precipitated from an aqueous solution of $H_3PW_{12}O_{40}$ using different reagents, such as Cs₂CO₃, CsCl or CsNO₃. However, the application of Cs₂CO₃ as the precipitating agent yielded material of extremely low specific surface area. Several researchers reported, that such prepared Cs₂HPW₁₂O₄₀ 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 Cs₂HPW₁₂O₄₀ 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 Cs₂HPW₁₂O₄₀ salt were improved, when instead of Cs₂CO₃ reactant, the CsCl was applied as precipitating agent. The so-obtained Cs₂HPW₁₂O₄₀ 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 Cs₂HPW₁₂O₄₀ 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 Cs₂HPW₁₂O₄₀ 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_{2.1}H_{0.9}PW₁₂O₄₀ 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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of these materials, no explanation concerning the role of cation has been reported. According to Okamoto et al. [17] and Inumaru [18] the mechanism of the formation and growth of polyoxometalates $M_3PW_{12}O_{40}$ (where $M = Cs^+$, Ag^+ , NH_4^+) aggregates is still unclear and needs further examination. The course of nanocrystals formation was suggested to be a self-organization process consisting of three subsequent steps; formation of nanocrystallites, self-assembly process to form aggregates and growth of particles by the attachment of other nanocrystallites. The course of such processes was observed to be strongly affected by the composition of solution and in particular by the nature of countercations (Cs⁺, Ag⁺, NH₄⁺) i.e. variables determining the dissolution/reprecipitation processes.

Due to the interesting effects described above, our recently performed studies [14] were extended to the use of CsBr and CsI as precipitating agents for the preparation of $Cs_2HPW_{12}O_{40}$ salt. The influence of ions existing in the solution during precipitation process on the physicochemical and catalytic properties of the $Cs_2HPW_{12}O_{40}$ salt was also studied. The 'as synthesized' samples were characterized by BET, FT-IR, XRD and SEM techniques. Their thermal stability (after annealing at 573 K for 2 h) was determined with BET, FT-IR and XRD methods. The catalytic activity of the $Cs_2HPW_{12}O_{40}$ samples was tested in the pore-sensitive transformation of m-xylene. Catalytic performance of so-obtained samples was compared with those of $Cs_2HPW_{12}O_{40}$ samples prepared using Cs_2CO_3 and CsCl as well as with that of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt precipitated using cesium carbonate.

2. Experimental

2.1. Preparation procedure

A commercially available 12-tungstophosphoric acid $(H_3PW_{12}O_{40}.24H_2O, HPW, Sigma-Aldrich)$ and Cs_2CO_3 (Aldrich), CsCl (POCh S.A), CsBr (Fluka) and CsI (Aldrich) were used to prepare the Cs₂HPW₁₂O₄₀ samples. In standard procedure the stoichiometric quantities of cesium carbonate (0.4 M) or other cesium salts (CsCl, CsBr, CsI) were added to the aqueous solutions of HPW (0.1 M). Then, the obtained colloidal solutions of precipitated samples were slowly evaporated to dryness overnight in the oven at 313 K. The Cs₂HPW₁₂O₄₀ samples precipitated with Cs₂CO₃, CsCl, CsBr and CsI were denoted as Cs₂(C), Cs₂(Cl), Cs₂(Br) and Cs₂(I), respectively. For the comparison, the Cs_{2.5}H_{0.5}PW₁₂O₄₀ salt was also precipitated using cesium carbonate (denoted in the text as Cs_{2.5}(C)).

2.2. Characterization of the catalysts

2.2.1. FT-IR spectroscopy

The FT-IR spectra were recorded using Nicolet 380 FT-IR spectrometer with standard KBr pellets technique. Prior to measurements, the samples were dried at 363 K in order to remove crystallization water.

2.2.2. XRD diffraction patterns and Rietveld refinement

The X-ray diffraction patterns obtained at ambient temperature were recorded in the range of $2\Theta = 5-90^\circ$, step size 0.02° and 12 s/step using the Siemens D5005 diffractometer (CuK α 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 overnight at 363 K. Full-matrix Rietveld refinement performed by TOPAS program was applied to calculate lattice parameters *a* and crystallite sizes of cesium samples [19,20]. As a starting model, H₃PW₁₂O₄₀·6H₂O (space group *Pn-3m* (224)) modified by replacing the H₅O₂⁺ by the cesium cations in [1/4, 1/4, 3/4] position, was used. This followed Brown et al. [1] who postulated that each cesium cation must replace one $H_5O_2^+$ ion. All crystal planes were taken into account in the Rietveld refinement because in this "ab-initio" method the diffractogram is fitted using the structure of the phase. The crystal-lite sizes were calculated using the L_{Vol} -IB method.

2.2.3. Surface area and porosity measurements

The specific surface areas of the $Cs_2HPW_{12}O_{40}$ samples as well as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt were calculated using the BET method. The nitrogen adsorption–desorption isotherms were obtained at 77 K using an Autosorb-1 (Quantachrome equipment). Prior to the measurements, the samples were preheated and degassed under vacuum at 473 K for 2 h. The micropores area of studied samples was calculated by t-micropore analysis. The pore size distribution in studied samples was obtained using BJH method.

2.2.4. Scanning electron microscopy and X-ray energy dispersive spectroscopy

The studies of the morphology of cesium samples were carried out by means of the JEOL JSM - 7500F Field Emission Scanning Electron Microscope with the EDXS (energy dispersive X-ray spectroscopy) detection system of characteristic X-ray radiation. The K575X Turbo Sputter Coater was used for coating the specimens with chromium.

2.2.5. Thermal stability

The 'as synthesized' $Cs_2(Cl)$, $Cs_2(Br)$ and $Cs_2(I)$ samples were annealed at 573 K for 2 h in the air atmosphere. The annealed samples are denoted as $Cs_2(Cl)$ -573 K, $Cs_2(Br)$ -573 K and $Cs_2(I)$ -573 K, respectively. Their structures as well as textural properties were investigated with FT-IR, XRD and BET methods.

2.2.6. Determination of acid sites strength

Acid sites strength was determined with Hammett indicators by means of procedure used by other authors [21,22]. Approximately 25 mg of sample was shaken with 1 cm³ of a solution of Hammett indicators diluted in methanol and left to equilibrate for 2 h after which no further color changes were observed. The color of the sample was then noted. The following Hammett indicators were used: 4-(dimethylamino)azobenzene (pKa = +3.3), 4-phenylazodiphenylamine (pKa = +1.5), crystal violet (pKa = +0.8), dicinnamalacetone (pKa = -3), anthraquinone (pKa = -8.2), 4nitrotoluene (pKa = -11.35), 3-nitrotoluene (pKa = -11.99), 1-chloro-4-nitrobenzene (pKa = -12.70), 1-chloro-3-nitrobenzene (pKa = -13.16), 1.4-dinitrotoluene (pKa = -13.75). The acid strength was quoted as being stronger than the weakest indicator which exhibited a color change but weaker than the strongest indicator that gave no change. The measurements of acid sites strengths were performed for the 'as synthesized' Cs₂(Cl), Cs₂(Br) and $Cs_2(I)$ as well as for the annealed $Cs_2(Br)$ -573 K and $Cs_2(I)$ -573 K samples.

2.3. Catalytic experiments

The transformation of m-xylene was performed in a tubular down-flow stainless steel reactor with 100 mg of catalyst (200–315 μ m fraction) and 2 cm³ of SiC chips (>400 μ m fraction). The catalysts were activated in helium flow at 573 K for 1 h. The tests were carried out in temperature range of 498–548 K in flowing helium and in the pulse mode, in order to avoid an excess of coke formation.

The analysis of substrate and products was performed by a Hewlett-Packard 6890 gas chromatograph connected on-line to the microreactor system, using a packed column (3 m, 2.0 mm i.d.) with



Fig. 1. FT-IR spectra of 'as synthesized' and annealed Cs₂(Br) and Cs₂(I) samples.

8% Bentone-34, 6% didecyl phthalate and 1% silicon oil A on Chromosorb W (60–80 mesh) and a TCD detector. The response factors of the detector were established using the appropriate aromatic hydrocarbons (reagent grade) and their mixtures as the standards. All reaction parameters were kept constant during the catalytic tests to maintain maximum reproducibility. Carbon and mass balances were kept below $\pm 5\%$.

3. Results and discussion

All samples were precipitated at $pH \cong 1$ because this factor strongly influences the formation of various heteropolyacid structures [23]. The structure of the 'as synthesized' $Cs_2(Br)$ and $Cs_2(I)$ samples was verified by FT-IR and XRD methods. The FT-IR spectra displayed in Fig. 1 confirmed that Keggin structure remained intact in prepared samples.

On all FT-IR spectra the set of bands located at 1079, 985, 888 and at ca. 800 cm^{-1} can be seen (Fig. 1). They are characteristic for Keggin unit and originate from the stretching vibrations of P–O_i, W=O_t, W-O_c-W or W-O_e-W, where oxygen within Keggin anions is denoted as O_i (internal), O_t (terminal), O_c (corner-sharing) and O_e (edge-sharing), respectively. The strong band located at 1079 cm⁻¹ associated with the presence of the $[PW_{12}O_{40}]^{3-}$ anion is clearly visible in the spectra of both $Cs_2(Br)$ and $Cs_2(I)$ samples, whereas no bands originating from other heteropolyacid structures appears. The band composed of two superimposed maxima at 993 cm⁻¹ and 985 cm⁻¹ can be assigned to the W=O group interacting with Cs⁺ and H₃O⁺ ions, respectively. This splitting is characteristic for acidic cesium salts [24,25] and was previously also observed in the spectra of K, Ag and Tl salts of HPW [26]. Taking into account previously reported FT-IR spectra for $Cs_2(C)$ and $Cs_2(Cl)$ samples [14], it can be stressed that for all studied samples of the Cs₂HPW₁₂O₄₀ salt, the Keggin structure is preserved independently of used precipitating agent.

The FT-IR spectra were also recorded for the $Cs_2(Br)$ -573 K and $Cs_2(I)$ -573 K samples, which were obtained after annealing at 573 K for 2 h, i.e. at the temperature used for their thermal pre-treatment prior to catalytic tests. As seen in Fig. 1 the positions



Fig. 2. XRD diffraction patterns of 'as synthesized' and annealed $Cs_2(Br)$ and $Cs_2(I)$ samples.

of bands characteristic for Keggin anion does not change and their intensities are almost the same as those observed in the spectra of the 'as synthesized' samples.

The XRD diffraction patterns registered for 'as synthesized' $Cs_2(Br)$ and $Cs_2(I)$ samples (Fig. 2) are in good agreement with this obtained for the $C_2HPW_{12}O_{40}$ salt, precipitated with a common procedure using Cs_2CO_3 [27,28], as well as with this of $Cs_2(Cl)$ reported in our previous paper [14]. Moreover, diffractions patterns recorded for the annealed $Cs_2(Br)$ -573 K and $Cs_2(I)$ -573 K samples are almost identical as those of the 'as synthesized' samples (Fig. 2). It can be also underlined that no reflections originating from other forms of heteropoly acid are observed. This demonstrates that the crystal structure of studied $Cs_2(Br)$ and $Cs_2(I)$ samples is stable up to 573 K. Similar data was reported by Okuhara et al. [27] for the $Cs_2(C)$ sample evacuated at 573 K. Details concerning structural parameters of both investigated samples are presented in Table 1.

The lattice parameters *a* are the same for the 'as synthesized' $Cs_2(Br)$ and $Cs_2(I)$ samples and they agree with the values of parameter *a* reported in our previous paper for $Cs_2(CI)$ and $Cs_2(C)$ samples (1.1879 nm and 1.1882 nm, respectively) [14]. Moreover, these values are also in good agreement with the other literature data [27,28]. As seen in Table 1, the size of crystallites is similar in the 'as synthesized' $Cs_2(Br)$ and $Cs_2(I)$ samples, 13.8 and 14.5 nm, respectively. However, they are smaller than those of the $Cs_2(C)$ and $Cs_2(CI)$ samples, 20 and 25 nm, respectively [14]. Although the crystallite sizes vary to some extent, there is no clear relationship between the type of used precipitating agent and calculated size of crystallites.

A thermal treatment of the $Cs_2(Br)$ and $Cs_2(I)$ samples does not induce essential changes in the lattice parameter *a* (Table 1) similarly as in the $Cs_2(CI)$ sample annealed at 573 K [14]. Alike, other authors did not observe changes for the $Cs_2(C)$ sample thermally treated under vacuum (573 K [27]) and (473 K [28]). On the other hand, after calcination of the $Cs_2(Br)$ and $Cs_2(I)$ samples, their crystallite size increases to about 17 nm in both $Cs_2(Br)$ -573 K and $Cs_2(I)$ -573 K samples (Table 1). It can be suggested that the growth of crystallite sizes is caused by recrystallization process during annealing of the samples up to 573 K. Thus, it can be

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Structural parameters of 'as synthesized' and annealed Cs2(Br) and Cs2(I) samples.

Sample	Lattice parameter a [nm]	Crystallites size [nm]	Relative intensity (%) of reflections in proportion to $2\Theta = 26.01^{\circ} (222)$	
			$2\Theta = 10.54^{\circ} (011)$	$2\Theta = 30.12^{\circ} (004)$
Cs ₂ (Br) 'as synthesized'	1.1867	13.8	49.3	31.3
Cs ₂ (Br)-573 K	1.1852	17.1	51.3	29.9
Cs ₂ (I) 'as synthesized'	1.1862	14.5	45.3	31.1
Cs ₂ (I)-573 K	1.1852	17.0	47.5	30.2

concluded that during recrystallization process, the smaller crystallites are enlarged, what causes a decrease of a specific surface area of the annealed samples. Similar recrystallization process was also observed in the case of $Cs_2(Cl)$ sample annealed at 573 K [14].

Table 1 shows the examples of calculated relative intensities of the reflections at $2\theta = 10.54^{\circ}$ (0 1 1) and at $2\theta = 30.12^{\circ}$ (0 0 4), taking into account the intensity of the strongest reflection at $2\theta = 26.01^{\circ}$ (2 2 2) as the reference (100%). Slight differences between the 'as synthesized' samples and those after annealing at 573 K for 2 h are observed, what confirms the thermal stability of the crystalline structure in the investigated samples.

The nitrogen adsorption-desorption isotherms of the "as synthesized" $Cs_2(Br)$ and $Cs_2(I)$ samples are displayed in Fig. 3. They are quite different from that obtained for nonporous $Cs_2(C)$ sample but are similar to the isotherm observed for mesoporous $Cs_{2.5}(C)$ salt [25]. All these isotherms exhibit hysteresis loops and according to IUPAC classification are IV-H3 type, which is characteristic of disordered, lamellar pore structure with 'slit & wedge' shape pores. They can be observed mainly in the case of very wide capillaries having narrow openings and in the case of an interstice between the parallel plates. The H3 type isotherm was also previously observed for crystalline metal oxide aggregates of sheet-like shape [29]. It should be stressed that the nitrogen adsorption–desorption isotherm obtained for the $Cs_2(Cl)$ sample exhibited similar shape to the above discussed samples [14].

As seen in Fig. 3, the isotherms obtained for the annealed $Cs_2(Br)$ -573 K and $Cs_2(1)$ -573 K samples still exhibit hysteresis loops, characteristic for mesoporous structures. Thus, despite of the recrystallization process, which causes the increase in crystallite sizes, both thermally treated samples still possess mesoporous structure.

The textural characteristics of the 'as synthesized' and annealed $Cs_2HPW_{12}O_{40}$ samples were calculated from the nitrogen adsorption–desorption isotherms and collected in Table 2. For the clarity of discussion, some data obtained for $Cs_2(C)$ and $Cs_2(Cl)$ samples and presented in our previous paper [14] are also given.

The specific surface area of the $Cs_2(C)$ sample is as low as ca. 1 m²/g, whilst those of the $Cs_2(Br)$ and $Cs_2(I)$ samples are much larger, 48.5 m²/g and 39.5 m²/g respectively. The surface area of 78.2 m²/g for the $Cs_2(CI)$ sample, presented in our previous paper [14], is the highest among all three samples prepared with cesium halides. All of these surface areas are dramatically higher in comparison to that for the $Cs_2(C)$ sample. It can be also observed that the specific surface area, micropores and mesopores areas decrease when going from Cl to I (Table 2) whilst the contribution of mesopores area in the specific surface area increases in the following



Fig. 3. The nitrogen adsorption–desorption isotherms obtained for 'as synthesized' and annealed $Cs_2(Br)$ and $Cs_2(I)$ samples. The isotherms for $Cs_2(CI)$ and $[Cs_2(CI)+HBr]$ samples as well as for the $Cs_2(C)$ and $[Cs_2(C)+HBr]$ samples are also presented.

Table	2
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Sorption properties of $\mathrm{Cs_2HPW_{12}O_{40}}$ salt precipitated with different reagents.

Sample	Ionic radius of halogen ^a [nm]	Surface area [m ² /g]	Micropores area ^{**} [m ² /g]	Micropores volume** [cc/g]	Mesopores area [m²/g]	Mesopores area/specific surface area [%]
Cs ₂ (C) ^b		1	-	-	-	_
Cs ₂ (Cl) ^b	0.167	78.2	33.2	0.017	45.0	57.5
Cs ₂ (Cl)-573 K		4.2	1.3	0.006	2.9	69.0
Cs ₂ (Br)	0.182	48.5	6.4	0.005	42.1	86.8
Cs ₂ (Br)-573 K		24.9	6.3	0.004	18.6	74.7
Cs ₂ (I)	0.206	39.3	3.2	0.003	36.1	91.9
Cs ₂ (I)-573 K		30.0	6.3	0.004	23.7	79.0
$[Cs_2(Cl) + HBr]$		73.1	8.2	0.010	64.9	88.8
[Cs ₂ (Cl)+HBr]-573 K		39.8	16.8	0.015	23.0	57.8

The values denoted (**) were calculated by t-micropore analysis.

^a Data from Ref. [30].

^b Data from Ref. [14].

order Cl < Br < I. A similar dependence is observed in the case of the annealed samples (Table 2). This is important from catalytic point of view.

The pore size distribution diagrams (Fig. 4) demonstrate that $Cs_2(Br)$ and $Cs_2(I)$ samples exhibit mesoporous structure. In both samples apart from the mesopores of 3.8 nm in diameter, also the wider ones of diameter within 6–10 nm significantly contribute to their porous structure. It is also interesting that the pore size of 3.8 nm observed in the $Cs_2(Br)$ and $Cs_2(I)$ samples is similar to pore size of 3.6 nm existing in the structure of $Cs_{2.5}(C)$ salt. According to Okuhara et al. [27] the structure of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt is consisted of the mesopores with voids and necks. The size of the latter is about 3 nm in width. Therefore, the formation of mesopores of such shape cannot be excluded in the samples of $Cs_2HPW_{12}O_{40}$ salt precipitated by cesium halides. However, it was previously described that in the $Cs_2(CI)$ sample the micropores (ca. 1.6 nm) and mesopores (6.2 nm) exist [14].

Above analysis confirms that the application of the CsBr or CsI reagent as the precipitating agents results in the $Cs_2HPW_{12}O_{40}$ samples with mesoporous structure, similar to that of the $Cs_{2.5}(C)$



Fig. 4. The pore size distribution diagrams for 'as synthesized' and annealed $Cs_2(Cl)$, $Cs_2(Br)$, $Cs_2(l)$ samples. The diagrams of $[Cs_2(C) + HBr]$ and $Cs_{2.5}(C)$ are also presented.

salt. All the results also clearly show that the type of halogen ion plays an important role in textural properties of the $Cs_2HPW_{12}O_{40}$ salt. To confirm the influence of the type of halogen ions on the formation of mesoporous structure of the $Cs_2HPW_{12}O_{40}$ salt, additional experiments were performed. To the colloidal solution of $Cs_2(C)$ and $Cs_2(Cl)$ samples, the HBr acid (at the stoichiometric amount) was added and the obtained colloidal suspension was further treated by a common procedure.

The nitrogen adsorption-desorption isotherm of the $[Cs_2(C)+HBr]$ final sample significantly differs from the starting nonporous $Cs_2(C)$ salt (Fig. 3). Moreover, the isotherm of $[Cs_2(C)+HBr]$ sample is similar to those obtained for the samples precipitated with CsBr or CsI reactants with characteristic loops derived from the mesoporous structures. Thus, it can be stressed that a simple addition of HBr to $Cs_2(C)$ salt can entirely change its compact structure into mesoporous one. This structural modification is also reflected in the increase of specific surface area from $1 \text{ m}^2/\text{g}$ for 'as synthesized' $Cs_2(C)$ salt to $34.8 \text{ m}^2/\text{g}$ observed for the $[Cs_2(C)+HBr]$ sample.

In the case of the $Cs_2(Cl)$ and $[Cs_2(Cl) + HBr]$ samples the nitrogen adsorption-desorption isotherms obtained for both samples are almost identical (Fig. 3). The specific surface area of [Cs₂(Cl)+HBr] sample is close to that of the Cs₂(Cl) salt, 73.1 and 78.2 m²/g, respectively. However, interesting changes of the textural properties are observed after addition of HBr to the colloidal solution of the Cs₂(Cl) salt (Table 2). The significant decrease of micropores area from 33.2 to $8.2 \text{ m}^2/\text{g}$ accompanied by the increase of mesopores area from 45.0 to $64.9 \text{ m}^2/\text{g}$ can be noticed. It means that the presence of bromide ions in the colloidal solution of the Cs₂(Cl) salt strongly influences the porosity of the obtained sample. It is also confirmed by the ratio of mesopores area/surface area calculated for the [Cs₂(Cl)+HBr] sample, which is higher than that for parent Cs₂(Cl) salt, 88.8 and 57.5%, respectively. On the other hand, this ratio obtained for the former is almost the same as that for the Cs₂(Br) salt, 86.8% (Table 2).

Interesting results were obtained after annealing of $[Cs_2(Cl)+HBr]$ sample at 573 K, evidenced by the decrease of surface area from 73.1 to $39.8 \text{ m}^2/\text{g}$. Moreover, the micropores area increased from 8.2 to $16.8 \text{ m}^2/\text{g}$ whilst the mesopores area decreased from 64.9 to $23 \text{ m}^2/\text{g}$ (Table 2). This change of porosity can be caused by the removing of bromide ions from the sample during annealing. It should be underlined that the treatment of sample before BET measurements i.e. 473 K for 2 h in vacuum can cause also partial removal of bromide ions. Especially, it can influence the porosity of 'as synthesized' sample. Despite that it can be concluded that the presence of HBr in the colloidal solution of $Cs_2(Cl)$ salt influences the formation of final sample and in this way its textural properties.

The ICP-AES method was applied to determine the contents of halogen in studied samples. The Br/Cs and I/Cs atomic ratios in 'as

synthesized' $Cs_2(Br)$ and $Cs_2(I)$ samples were close to the stoichiometric ratio being near to 1. After annealing the samples at 353 and 573 K both atomic ratios decreased dramatically to about 0.046 and 0.012, respectively. It demonstrates that already during heating at 353 K almost all bromide or iodide ions were removed. These results clearly confirm the previous conclusion that halogen ions play a vital role in the formation of porous structure of studied samples during their synthesis.

The morphology of $Cs_2(Br)$, $Cs_2(I)$, $[Cs_2(C) + HBr]$ and $Cs_{2.5}(C)$ samples was studied by scanning electron microscopy technique and obtained micrographs are displayed in Fig. 5. All samples, which are characterized by mesoporous structure, form spherical particles consisting of much smaller primary particles. The Cs₂(Cl) sample also exhibits similar morphology, showing loosely aggregated almost spherical particles composed of small nanocrystallites [14]. Hence, the morphology of all samples prepared with cesium halides differ entirely from that of the $Cs_2(C)$ sample but is similar to that of the Cs_{2,5}(C) salt [14,27]. According to the literature data [27] and our previous results, a highly compact structure of the $Cs_2(C)$ sample possesses smooth surface and any primary particles cannot be noticed. However, the $Cs_2(C)$ salt after addition of HBr can completely change its morphology because of the formation of spherical particles composed of aggregated primary particles which are observed in $[Cs_2(C) + HBr]$ sample (Fig. 5). It can be supposed that after the precipitation process of the Cs₂(C) sample, the Br⁻ ions can penetrate and decompose its compact structure and after self-organization process, can form mesoporous structure consisting of spherical particles. This shows how halides ions can influence the formation of mesoporous structure of Cs₂HPW₁₂O₄₀ salt.

Our previous studies [14] showed that Cl^- ions were easily removed from the 'as synthesized' $Cs_2(Cl)$ sample. It was demonstrated that this sample was 'free' of chloride ions after heating at 453 K. The Cl atoms were also not detected by EDXS-SEM technique. This suggested that vacuum pre-treatment of the sample prior to microscopic studies caused the release of chloride ions. In the case of $Cs_2(Br)$ and $Cs_2(I)$ samples expected values of Br and I atoms were equal to about 5 and 8 wt%, respectively. However, their content detected by EDXS measurements was much lower. It has been assumed that Br and I ions stayed to some extent in the structures of both samples because their higher atomic masses compared to chloride ions. This is consistent with the ICP-AES results presented above which showed much higher content of halogens in the 'as synthesized' samples and practically lack of halogens after their annealing at 573 K.

The role of halogen ions could be explained using a model described by Okuhara et al. [27] which suggested that the pore structure of $Cs_xH_{3-x}PW_{12}O_{40}$ salt precipitated with Cs_2CO_3 was greatly dependent on the Cs/Keggin anion ratio. The final texture of these samples was formed via slow aggregation of primary crystallites during heating and evaporation of the solution. The crystalline sample of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was consisted of loosely aggregated fine crystallites forming both micro- and mesopores. In contrast, the $Cs_2HPW_{12}O_{40}$ salt (prepared with Cs_2CO_3) was consisted of dense aggregates of fine crystallites, what resulted in a lack of porosity.

According to our previous results, at the beginning of acidic cesium salts precipitation in water solution, primary particles are formed and their surfaces are enriched by the protons [31,32]. When the Cs₂HPW₁₂O₄₀ salt is precipitated by Cs₂CO₃ gaseous CO₂ is liberated from the colloidal solution, whilst when CsCl, CsBr or CsI are used as the reagents, the HCl, HBr or HI may stay in the solution influencing the aggregation of primary particles. Therefore, the interaction of Cl⁻, Br⁻ or l⁻ ions with surface protons of primary particles should be taken into consideration. When ionic radius increases from Cl⁻ to l⁻ (Table 2), the energy of H–Cl > H–Br > H–I bond decreases (432, 366 and 298 kJ/mol, respectively [33]). It can

be expected that interactions of Cl⁻ ions with the surface protons of primary particles could be the strongest whereas those of l⁻ ions the weakest. It was previously showed that the addition of chloride ions to the Cs₂(C) sample strongly influenced its structure [14]. The presence of chloride ions in the colloidal solution of [Cs₂(C) + HCl] or Cs₂(Cl) samples caused the formation of larger colloidal particles in both cases [14]. This could be a result of interactions of chloride ions with primary particles of these samples before aggregation process or penetration of chloride ions into already formed colloidal particles of the Cs₂(C) sample. Similar phenomenon was observed after addition of HBr to the Cs₂(C) sample.

However, the addition of HBr to the colloidal solution of $Cs_2(CI)$ sample practically did not change the specific surface area whereas some changes in the porosity appeared, as was described above (Table 2). Because the energy of H—Cl bond is much higher than that of H—Br bond the exchange of chloride ions by bromide ions can be excluded. It seems that the results obtained for the $[Cs_2(CI) + HBr]$ sample can indicate the co-absorption of bromide ions, when they are present in the colloidal solution. This could be a result of the penetration of bromide ions into colloidal particles. Such process could change the porosity of $[Cs_2(CI) + HBr]$ sample, which is reflected by the increase of mesopores area accompanied by the decrease of micropores area. However, this phenomenon seems to be more complicated and its detailed explanation requires further studies.

Thus, it seems to be obvious that halide ions play an important role in the aggregation of primary particles influencing the formation of mesoporous structure of the studied samples. On the other hand, taking into account the ionic radius of halogens (Table 2), it is easy to explain how they influence the porous structure of the $Cs_2HPW_{12}O_{40}$ salt. The presence of the smallest Cl^- ions causes that the structure with the highest contribution of micropores is formed. When Br^- or I^- ions interact with primary particles in $Cs_2(Br)$ and $Cs_2(I)$ samples, the aggregated structure of the highest contribution of mesopores is created (Table 2).

After calcination of the Cs₂(Cl), Cs₂(Br) and Cs₂(I) samples at 573 K for 2 h, their specific surface area decreases and also some changes in the pore distribution diagrams can be observed (Fig. 4). Thermal treatment induces the most dramatic changes in the structure of the Cs₂(Cl) sample. Strong reduction in surface area (from 78.2 to $4.2 \text{ m}^2/\text{g}$) is accompanied by remarkable changes in the porous structure. As Fig. 4 shows, wide mesopores with the maximum of about 6.2 nm in diameter vanish almost completely after calcination, whereas some new narrower mesopores of 3.8 nm in diameter are created. For the annealed Cs₂(Br) and Cs₂(I) samples, the micropores structure (volume and area) practically does not change and mesopores of 3.8 nm in diameter are preserved. The contribution of the larger mesopores, of diameter within 6-10 nm range, decreases to some extent especially in the case of Cs₂(Br) sample. For the latter sample, ca. two-fold decrease in surface area appears (from 48.5 to 24.9 m²/g). The changes are definitively less pronounced for the Cs₂(I) sample as its surface decreases only slightly from 39.3 to $30.0 \text{ m}^2/\text{g}$. The recrystallization process resulting in the formation of larger crystallites (Table 1) may be responsible for the observed structural changes. Alike, the mesopores of 3.6 nm in diameter are present in the Cs_{2.5}H_{0.5}PW₁₂O₄₀ salt (Fig. 4). As previously described, the mesoporous structure of the $Cs_{2,5}(C)$ is stable under heating at 573 K in vacuum [27]. Data presented by Zhang et al. [34] demonstrated that the mesoporous structure of $Cs_xH_{3-x}PW_{12}O_{40}$ samples with $x \ge 2.2$ did not change even after catalytic reaction performed at 653 K.

At this point, a question may be raised as to why the mesopores of 3.6-3.8 nm in diameter are resistant for annealing at 573 K in $Cs_2(Br)$, $Cs_2(I)$ as well as in $Cs_{2.5}(C)$ samples. It was reported that in the structure of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt the closest packed aggregates formed the voids and necks, the latter with the size of about



Fig. 5. The representative SEM images of prepared samples of Cs₂HPW₁₂O₄₀ and Cs_{2.5}H_{0.5}PW₁₂O₄₀ salts (magnification of 100,000).

3 nm [27]. In turn, here in cesium halide-derived $Cs_2HPW_{12}O_{40}$ samples the mesopores of ca. 3.8 nm as well as the wider mesopores of 6–10 nm are observed (Fig. 4). The former may be related to the closest packed aggregates similarly to what is proposed for the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt. These mesopores are resistant for annealing at 573 K. The latter can be ascribed to loosely sticking primary particles, which form thermally unstable structure. In the case of $Cs_2(Cl)$ sample, the formation of the closest packed aggregates after heating at 573 K probably is the reason that mesopores with 3.8 nm in diameter are created.

The catalytic activity of studied cesium salts was tested in the transformation of m-xylene which is catalyzed by acid centers (Scheme 1). Therefore, the acid sites strength of studied samples was determined with Hammet indicators by means of procedure used by other authors [21,22]. In both Cs₂(Br) and Cs₂(I) samples the strength of acid centers was determined as $-13.2 < H_0 < -13.8$, what corresponds with the data reported by Okuhara et al. for Cs₂(C) and Cs_{2.5}(C) samples [21]. Similar acid sites strength was determined also for the 'as synthesized' Cs₂(Cl) as well as for the annealed Cs₂(Br)-573 K and Cs₂(I)-573 K samples.

Transformation of m-xylene is frequently studied as a model reaction for zeolites and molecular sieves *e.g.* catalysts of various porosity characteristics [35]. Thus, the catalytic performance of the Cs₂(Cl), Cs₂(Br) and Cs₂(I) samples was compared with those of the Cs₂HPW₁₂O₄₀ and Cs₂.5H_{0.5}PW₁₂O₄₀ salts prepared by a common procedure using Cs₂CO₃ and exhibiting surface area of 1 m²/g and 136.7 m²/g, respectively. The obtained conversion of m-xylene against reaction time is plotted in Fig. 6. As described in Section 2, before the catalytic test the samples were activated at 573 K for 2 h.

The obtained data show that $Cs_2(C)$ sample of nonporous structure is inactive. The $Cs_2(C)$ sample exhibits very low activity and the conversion of m-xylene attains 3% only at reaction temperature as high as 573 K. This low activity may be ascribed to very low specific surface area of the $Cs_2(Cl)$ -573 K sample (4.2 m²/g, Table 2) due to highly compact structure. In turn, after thermal activation of the Cs₂(Br) and Cs₂(1) samples, their mesoporous structures are partially preserved and both catalysts are active under used conditions of catalytic test. These samples possess the pore structure characterized by the predominant pore diameters of 3.8 nm (Fig. 4), which is high enough to accommodate the m-xylene molecule of 0.64 nm in size. Alike, the Cs_{2.5}(C) salt with the mesoporous structure consisting of pore of 3.6 nm in diameter is also active in investigated reaction.



Fig. 6. Comparison of catalytic activity of $Cs_2(Br)$, $Cs_2(I)$ and $Cs_{2.5}(C)$ samples. The conversion of m-xylene as a function of reaction temperature.



Scheme 1. Simplified reaction scheme of m-xylene transformation.

As Fig. 6 demonstrates within the whole temperatures range, the $Cs_2(Br)$ and $Cs_2(I)$ are much more active catalysts than the $Cs_{2,5}(C)$ salt, which is generally considered to be excellent 'superacid' catalyst. At reaction temperature of 498 K the activity of Cs₂(Br) and $Cs_2(I)$ is about 3 times higher than that of $Cs_2(C)$ salt. At higher temperatures, 523 K and 548 K, this ratio attains about 2.1 and 1.6, respectively. Consequently, the activities of Cs₂(Br) and Cs₂(I) samples are roughly estimated to be about two-fold higher than that of the $Cs_{2,5}(C)$ salt. As the mass of catalysts in the reactor is practically the same, this clearly demonstrates two-fold higher activity of the Cs₂HPW₁₂O₄₀ salt, synthesized with CsBr or CsI reagent, per 1 g of catalyst than that of the Cs_{2.5}H_{0.5}PW₁₂O₄₀ salt. Taking into account comparable strength of acid sites in the studied catalysts, the obtained almost quantitative activity relation may be explained by a two-fold higher number of active centers (protons) in the $Cs_2HPW_{12}O_{40}$ compared to that in the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt. It should be also underlined that the catalytic activity of $[Cs_2(C) + HBr]$ sample is similar to that of $Cs_2(Br)$ salt.

In the transformation of m-xylene three main reactions pathway can be generally observed: isomerization to *para-* and *orto*xylene, disproportionation into toluene and trimethylbenzenes and dealkylation to form benzene and toluene [36]. The products of all these reactions were observed in the presence of studied cesium salts. The ratio of p/o-xylene isomers, the selectivity of isomerization versus disproportionation and the distribution of trimethylbenzenes isomers are the experimental values commonly considered to be indications of diffusion restrictions (pore-size and pore-shape limitations) being a result of pore structure in the catalyst [37].

The p/o-xylene ratio is predicted by the thermodynamic equilibrium to be 1.05 (at 623 K) [37]. The higher values reflect the difference in diffusion of these compounds, due to poresize limitations. m-Xylene disproportionation being a bimolecular reaction involving bulky trimethyldiphenylmethane intermediates occurs only when an intermediate molecule can be accommodated into the pores, as in the case of zeolites with supercages of $0.71 \text{ nm} \times 1.84 \text{ nm}$ in size. In the presence of all three Cs₂(Br), Cs₂(I) and Cs_{2.5}(C) samples the p-/o-xylene ratio is ca. 1.0 what clearly indicates a lack of diffusion restrictions in all studied cesium salts.

The selectivities of m-xylene transformation by isomerization, disproportionation and dealkylation pathways were determined to be 28.5–30.8%, 57.5% and 14.0–11.7% (at 548 K), respectively. All of them are of similar order as the values obtained in the presence of other catalysts when no "reagents-molecule size" restrictions were operative, *e.g.* faujasite [35]. The selectivity of isomerization versus

that of disproportionation was determined to be 0.5 on all cesium salts, being of similar order to that on HY zeolite [37]. The ratio of 1,2,3- to 1,3,5-trimethylbenzenes was equal to 0.29 (at 548 K), being close to the thermodynamic equilibrium value of 0.33. This is an analogous relation as that observed in the presence of faujasite and Linde type SK-45 zeolite [35]. It also shows that the available void volumes in the structure of Cs₂(Br), Cs₂(I) and Cs_{2.5}(C) catalysts are sufficient to accommodate the trimethyldiphenylmethane an intermediate complex of the disproportionation reaction. Thus, similar selectivity pattern on zeolites and on Cs₂(Br), Cs₂(I) as well as Cs_{2.5}(C) catalysts clearly shows that the openings in mesopores existing in studied cesium salts could not be narrower than those in the above mentioned zeolites (window sizes of 0.735 and 0.750 nm, respectively) [38,39].

4. Conclusions

The samples of Cs₂HPW₁₂O₄₀ salt were precipitated with CsCl, CsBr, CsI and with a common procedure using Cs₂CO₃. The use of cesium halides as precipitating agent causes the formation of loosely aggregated, partially mesoporous structures of the Cs₂HPW₁₂O₄₀ samples. The type of halogen ions influences the contribution of mesopores in the Cs₂HPW₁₂O₄₀ samples, which increases when the atomic size of halogen grows in the order Cl < Br < I. It is also suggested that interaction of halogen ions with the surface protons of primary particles, before their aggregation affects the formation of mesoporous structure. The textural and morphological features of so-obtained samples are similar to those of the Cs_{2.5}H_{0.5}PW₁₂O₄₀ salt.

Thermal treatment of cesium halides-derived $Cs_2HPW_{12}O_{40}$ samples at 573 K for 2 h changes their mesoporous structures to some extent only. After calcination the wider mesopores (6–10 nm) vanish almost completely. In $Cs_2(Br)$ and $Cs_2(I)$ samples the mesopores of 3.8 nm in diameter are still present whereas in the case of the $Cs_2(CI)$ sample they appeared. Thus, the texture of the $Cs_2(Br)$ and $Cs_2(I)$ samples and their thermal stability are quite similar to the $Cs_{2.5}(C)$ salt, which is an active catalyst in many reactions.

Catalytic properties of all $Cs_2HPW_{12}O_{40}$ samples were investigated in the pore-size sensitive transformation of m-xylene and compared with that of the $Cs_{2.5}(C)$ salt. The $Cs_2(C)$ and $Cs_2(Cl)$ samples were inactive because of their low specific surface areas. However, the change of inactive $Cs_2(C)$ sample into active catalyst by simple modification of preparation procedure *i.e.* by the addition of HBr to its colloidal solution is possible. In contrast $Cs_2(Br)$ and $Cs_2(I)$ samples as well as $Cs_{2.5}(C)$ salt were active catalysts, however, the two former samples exhibited two-fold higher activity than the latter. Similar strength of acid sites in all active catalysts allows to conclude that the number of protons in the $Cs_2HPW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salts is a key factor influencing their catalytic activity in transformation of m-xylene.

References

- G.M. Brown, M.R. Noe-Spirlet, W.R. Busing, H.A. Levy, Acta Crystallogr. B33 (1977) 1038–1046.
- [2] M. Misono, Catal. Rev. Sci. Eng. 29 (2/3) (1987) 269-321.
- [3] Y. Izumi, Catal. Today 33 (1997) 371–409.
- [4] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
- [5] T. Okuhara, Chem. Rev. 102 (2002) 3641-3666.
- [6] M. Misono, Chem. Commun. (2001) 1141-1152.
- [7] J. Kaur, I.V. Kozhevnikov, Chem. Commun. (2002) 2508–2509.
- [8] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113-252.
- [9] J. Bonardet, J. Fraissard, G.B. McGarvey, J.B. Moffat, J. Catal. 151 (1995) 147-154.
- [10] G. Koyano, K. Ueno, M. Misono, Appl. Catal. A 181 (1999) 267-275.
- [11] P.Y. Gayraud, N. Essayem, J.C. Vedrine, Catal. Lett. 56 (1998) 35-41.
- [12] N. Essayem, S. Kieger, G. Coudurier, J.C. Vedrine, Stud. Surf. Sci. Catal. 101A (1996) 591–600.
- [13] B.B. Bardin, R.J. Davis, Top. Catal. 6 (1998) 77-86.
- [14] L. Matachowski, A. Drelinkiewicz, E. Lalik, D. Mucha, B. Gil, Z. Brożek-Mucha, Z. Olejniczak, Microporous Mesoporous Mater. 144 (1–3) (2011) 46–56.
- [15] D. Lapham, J.B. Moffat, Langmuir 7 (1991) 2273-2278.
- [16] T. Okuhara, Appl. Catal. A 256 (2003) 213-224.
- [17] K. Okamoto, S. Uchida, T. Ito, N. Mizuno, J. Am. Chem. Soc. 129 (2007) 7378-7384.
- [18] K. Inumaru, Catal. Surv. Asia 10 (2006) 151–160.

- [19] Bruker AXS (2003): TOPAS V2.1; General Profile and Structure Analysis Software for Powder Diffraction Data. – User's Manual, Bruker AXS, Karlsruhe, Germany.
- [20] R.W. Cheary, A.A. Coelho, J. Appl. Crystallogr. 25 (1992) 109–121.
 [21] T. Okuhara, T. Nishimura, H. Watanabe, M. Misono, J. Mol. Catal. 74 (1992)
- 247-256.
- [22] A.K. Singh, S.D. Fernando, Energy Fuels 22 (2008) 2067–2069.
- [23] Z. Zhu, R. Tain, C. Rhodes, Can. J. Chem. 81 (2003) 1044–1050.
- [24] N. Essayem, A. Holmquist, P.Y. Gayraud, J.C. Vedrine, Y.B. Taarit, J. Catal. 197 (2001) 273–280.
- S. Choi, Y. Wang, Z. Nie, J. Liu, C.H.F. Peden, Catal. Today 55 (2000) 117–124.
 M. Todorovič, I. Holclajtner-Antunovič, U. Mioč, D. Bajuk-Bogdanovič, Mater.
- Sci. Forum 55 (2007) 207–212.
- [27] T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru, M. Misono, Chem. Mater. 12 (2000) 2230-2238.
- [28] J.A. Dias, E. Caliman, S.C.L. Dias, Microporous Mesoporous Mater. 76 (2004) 221-232.
- [29] K. Kaneko, J. Membr. Sci. 94 (1994) 59-89.
- [30] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751-767.
- [31] A. Zięba, A. Drelinkiewicz, P. Chmielarz, L. Matachowski, J. Stejskal, Appl. Catal. A: Gen. 387 (2010) 13–15.
- [32] L. Matachowski, A. Zięba, M. Zembala, A. Drelinkiewicz, Catal. Lett. 133 (2009) 49–62.
- [33] http://www.webchem.net/data/BondEnthalpies.htm
- [34] J. Zhang, M. Sun, C. Cao, Q. Zhang, Y. Wang, H. Wan, Appl. Catal. A: Gen. 380 (2010) 87–94.
- [35] J.A. Martens, J. Perez-Pariente, E. Sastre, A. Corma, P.A. Jacobs, Appl. Catal. 45 (1988) 85-101.
- [36] S. Laforge, D. Martin, J.L. Paillaud, M. Guisnet, J. Catal. 220 (2003) 92-103.
- [37] P. Lourenco, M.F. Ribeiro, F. Ramoa Ribeiro, J. Rocha, Z. Gabelica, Appl. Catal. A 148 (1996) 167–180.
- [38] Ch. Baerlocher, W.M. Meier, D.H. Olson, Atlas of Zeolite Framework Types, fifth ed., Elsevier, Amsterdam, 2001.
- [39] http://www.iza-structure.org/databases/