

**60th International Conference for Students of Physics and Natural Sciences**

# **Open Readings 2017**

**March 14-17, 2017**

**Vilnius, LITHUANIA**

**Programme and Abstracts**

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# Ce-CONTAINING POLYOXOTUNGSTATES: SYNTHESIS, FTIR SPECTROSCOPY, AND SURFACE MICROMORPHOLOGY

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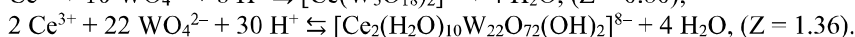
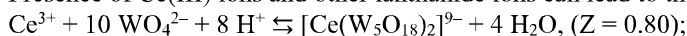
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Polyoxometalates are a class of metal oxide clusters of early transition metals (V, Mo, W, Nb, etc.), and they show strong Brønsted acidity, fast reversible multi-electron redox transformations under mild conditions, and adjustable acid-base and redox properties over a wide range. Therefore, the use of POMs as acidic and redox-bifunctional catalysts in homogeneous and heterogeneous systems is their most popular and important application area. Thus, cerium decatungstate  $[\text{Ce}^{\text{IV}}(\text{W}_5\text{O}_{18})_2]^{8-}$  modified with cetylpyridinium cations was found to be an active and selective catalyst for the oxidation of secondary alcohols to ketones with hydrogen peroxide [1].

In present work we have studied the interactions of cerium (III) chloride with aqueous solutions of  $\text{Na}_2\text{WO}_4$  at various acidity  $Z = v(\text{H}^+)/v(\text{WO}_4^{2-}) = 0 - 1.50$ . As known [2], during them isopoly tungstate anions of different composition  $[\text{H}_{m-2k}\text{W}_n\text{O}_{4n-k}]^{(2n-m)-}$  are formed.

Presence of Ce(III) ions and other lanthanide ions can lead to the formation of heteropoly anions [3-4]:



From aqua-acetone media ( $v/v = 50/50$ ) at  $Z = 0.80$  the sodium heteropoly decatungstocerate (III)  $\text{Na}_9[\text{Ce}(\text{W}_5\text{O}_{18})_2] \cdot 28\text{H}_2\text{O}$  with Peacock-Weakley anion structure was synthesized. From acidified up to  $Z = 0.80$  aqueous solution of sodium tungstate without acetone adding the acid sodium heteropoly decatungstocerate (IV)  $\text{Na}_6\text{H}_2[\text{Ce}(\text{W}_5\text{O}_{18})_2] \cdot 30\text{H}_2\text{O}$  with Peacock-Weakley anion structure was synthesized. Salts of these heteropoly compounds have different micromorphology (Fig. 1) and different positions of vibration maxima in the FTIR spectra (FTIR data for  $\text{Na}_9[\text{Ce}(\text{W}_5\text{O}_{18})_2] \cdot 28\text{H}_2\text{O}$ ,  $\text{cm}^{-1}$ : 416, 485, 542, 575, 711, 787, 845, 955; FTIR data for  $\text{Na}_6\text{H}_2[\text{Ce}^{\text{IV}}(\text{W}_5\text{O}_{18})_2] \cdot 30\text{H}_2\text{O}$ ,  $\text{cm}^{-1}$ : 436, 491, 553, 583, 677, 783, 828, 941).

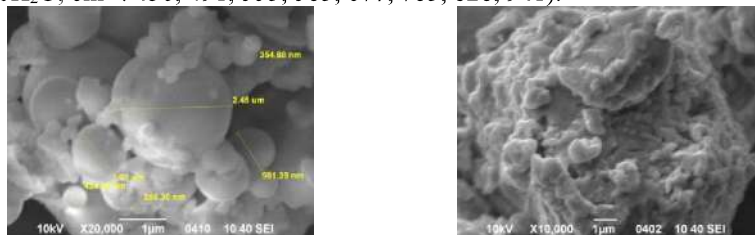


Fig. 1. SEM images of  $\text{Na}_9[\text{Ce}(\text{W}_5\text{O}_{18})_2] \cdot 28\text{H}_2\text{O}$  powder surface (left – 20,000 times magnification), and  $\text{Na}_6\text{H}_2[\text{Ce}(\text{W}_5\text{O}_{18})_2] \cdot 30\text{H}_2\text{O}$  (right – 10,000 times magnification)

From the solution with  $Z = 1.00$  the cerium heptatungstate  $\text{Ce}_2\text{W}_7\text{O}_{24} \cdot 20\text{H}_2\text{O}$  was synthesized, and by XRD it was shown that its thermal decomposition accompanied with crystallization of  $\text{Ce}_4\text{W}_9\text{O}_{33}$  and  $\text{WO}_3$  phases.

By the chemical analysis and FTIR spectroscopy it was shown that the  $\text{Ce}_5[\text{HW}_7\text{O}_{24}]_3 \cdot 56\text{H}_2\text{O}$  was synthesized from solution with  $Z = 1.17$ , and by XRD method it was shown that calcination of  $\text{Ce}_5[\text{HW}_7\text{O}_{24}]_3 \cdot 56\text{H}_2\text{O}$  at  $500^\circ\text{C}$  occurs with only  $\text{WO}_3$  phase crystallization, and calcination at  $700^\circ\text{C}$  accompanied with crystallization of  $\text{Ce}_4\text{W}_9\text{O}_{33}$  phase. By the chemical analysis and FTIR spectroscopy it was shown that the cerium paratungstates B –  $\text{Ce}_{10}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]_3 \cdot 94\text{H}_2\text{O}$  and  $\text{Na}_{10}\text{Ce}_{20}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]_7 \cdot 180\text{H}_2\text{O}$  were synthesized from equilibria solutions with  $Z = 1.17$  and  $1.29$ , respectively, and  $\text{Na}_2\text{Ce}_2[\text{Ce}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{72}(\text{OH})_2] \cdot 35\text{H}_2\text{O}$  with lacunar metatungstate-anions as ligands was synthesized from the solution at  $Z = 1.364$ .

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