



**CHISA**  
**2016**  
**PRAGUE**  
**PRES 2016**

22<sup>nd</sup> International Congress of Chemical  
and Process Engineering  
CHISA 2016

19<sup>th</sup> Conference on Process Integration,  
Modelling and Optimisation for Energy  
Saving and Pollution Reduction  
PRES 2016

organized by

**ČSChI** ČESKÁ SPOLEČNOST CHEMICKÉHO INŽENÝRSTVÍ  
CZECH SOCIETY OF CHEMICAL ENGINEERING

Prague, Czech Republic, 27 August - 31 August 2016



**CD-ROM - ABSTRACTS**

**Supported heteropoly acid catalysts of oxidative conversion of alkanes**

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Physical and chemical properties of heteropoly acids (HPA) at low-temperature oxidative catalysis and action of reaction medium were investigated enough. Such investigations are insufficient for high-temperature reactions. It makes difficult exposure the nature of a stable catalytic action of supported heteropoly compounds (HPC) at high-temperature processes including partial oxidative conversion. The experimental data on investigation of thermal stability and dynamics of charge and structural transformations of compact the 12<sup>th</sup> series P-Mo HPA and supported on SiO<sub>2</sub> in conditions of consecutive influence of components: O<sub>2</sub> of air at the presence water vapor, H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O at the temperatures of real oxidative processes (473-1273 K) are demonstrated.

15-30% HPA supported on SiO<sub>2</sub> have been prepared by impregnation of the carrier by water solutions of HPA on a moisture capacity with the subsequent drying on air at 383 K within 5 h. Physical and chemical properties of catalysts were investigated by complex of methods: XRD on DRON-407 device with the cobalt anode, and IR-spectroscopy - on SPECORD-75 spectrometer in KBr tablets. Spectra of thermal programmed reduction by hydrogen (TPR) and thermal programmed oxidation by oxygen (TPO) were detected by registration of absorbed H<sub>2</sub> or O<sub>2</sub> at 293-1273 K by chromatographic method with thermal conductivity detector at passing of Ar-5%H<sub>2</sub> (vol.) or He-5%O<sub>2</sub> (vol.) mixtures (40 sm<sup>3</sup>/min) and speed of the programmed rise of temperature - 8 K/min.

The received results allow to assume that the beginning of structural destruction of crystalline [PMo<sub>12</sub>] begins from  $\geq 773$  K (disappears characteristic a.b. 950 sm<sup>-1</sup> from Mo=O), MoO<sub>3</sub> phase is formed. Thus a.b. in the field of 1060-1150 sm<sup>-1</sup> from P-O-Mo (molybdophosphates) are kept up to 1073 K. However the subsequent processing of the sample by superheated steam at 923 K leads to renewal of all a.b. in the IR-spectrum, which are characteristic for Keggin type of HPA with high intensity (780,860,940,1060 sm<sup>-1</sup>). It is possible to assume that introduction of water vapor into a reaction mixture promotes "regeneration" of the Keggin structure of [PMo<sub>12</sub>] from a mixture of remained fragments after calcination (Mo-O-Mo, Mo/O\Mo - bridge, molybdophosphates) as due to reoxidation, and introductions of H<sub>2</sub>O molecules into Keggin skeleton with formation of fluidized structures. The role of water as oxidizer in the processes of partial oxidation and oxidative dehydrogenation of methane was established by a combination of isotope and kinetic methods in works. Thus, research of thermal stability of the [PMo<sub>12</sub>] and [PMo<sub>10</sub>V<sub>2</sub>] HPA in a steam-air mixture by IR-spectroscopy has shown, that it is steady at temperatures  $\leq 673$  K. The beginning of HPA destruction on oxide components (MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub>) together with intermediate oxide-like formations (P-O-Mo, V-O-Mo) is possible at the temperatures  $\geq 773$  K. Formation of MoO<sub>3</sub> phase and molybdophosphates with preservation of low-intensive HPA a.b. was observed at 1023 K. The subsequent processing of samples in water (superheated steam) after steam-air processing at 923, 1023 K leads to strongly pronounced "regeneration" of the Keggin structure of HPA (a.b. 780, 860, 960, 1050 sm<sup>-1</sup>) at preservation of low-intensive a.b. from MoO<sub>3</sub> (580, 870,980 sm<sup>-1</sup>). Further results of investigation on interaction of structural oxygen of catalysts with hydrogen (TPR method) on the base of

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compact and supported HPA are demonstrated. Thus, these stages of reduction of the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$  are reflected in occurrence in TPR spectra the peaks of hydrogen absorption at 573-773 K (reduction and decomposition of HPA), 773-1023 K (reduction of  $\text{MoO}_3$  into  $\text{MoO}_2$ ), 1023-1273 K (reduction of  $\text{MoO}_2$  into  $\text{Mo}^0$ ). Reoxidation process by oxygen of 30% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and 30% $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{SiO}_2$  catalysts at TPO regime after their preliminary reduction by hydrogen (TPR) to formation of  $\text{Mo}^0$  proceeds in the field of temperatures 473-1023 K with appearance of three absorption peaks of  $\text{O}_2$ :  $T_{\text{max}}$  - 593-603, 683-703, and 743-763 K for  $[\text{PMo}_{10}\text{V}_2]/\text{SiO}_2$  catalyst and  $T_{\text{max}}$  - 623-643, 703-723, and 803-823 K for  $[\text{PMo}_{12}]/\text{SiO}_2$  catalyst. It is visible that reoxidation is the more low-temperature process on 100-200 K, than reduction process of supported catalytic systems (12<sup>th</sup> series Mo HPA). From comparison of data on  $T_{\text{red}}$  and  $T_{\text{ox}}$  of molybdenum in  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{SiO}_2$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$  systems follows that introduction of vanadium into  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  structure leads to increase of interaction temperature with hydrogen of structural oxygen of supported HPA and temperature of formation of molybdenum oxides and  $\text{Mo}^0$ , but reduce reoxidation temperature of the reduced forms of molybdenum in comparison with  $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$  on 30-50 K. Partial replacement of molybdenum on vanadium in  $[\text{PMo}_{12}]$  HPA reduces the reduction speed (raises  $T_{\text{red}}$ ) of  $\text{Mo}^{6+} \rightarrow \text{Mo}^0$ , but increases the reoxidation speed (reduces  $T_{\text{ox}}$ ) of  $\text{Mo}^0$ , formed on the basis of HPC, into  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$  oxides. Thus, reversible transition of  $\text{Mo}^{6+}$  ( $\text{MoO}_3$ )  $\leftrightarrow$   $\text{Mo}^0$  is observed in catalysts from 12<sup>th</sup> series HPA on carrier under influence of oxidation-reduction components ( $\text{O}_2$ ,  $\text{H}_2$ ) at the temperature interval 773-1273 K. It predetermines an opportunity of carrying out of the reaction of partial oxidation of  $\text{C}_1$ - $\text{C}_4$  alkanes on the oxidation-reduction mechanism. It was established that the keeping of 30% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$  catalyst preliminary treated by TPR with hydrogen up to 923 K (there are  $\text{MoO}_3$ ,  $\text{MoO}_2$  phases) and TPO up to 873 K, or TPR with hydrogen up to 1273 K ( $\text{Mo}^0$ ) and TPO up to 1123 K in water leads to reduction of HPC structure on a surface of carrier. Thus we observe reversible cycle of structural and phase transformations of HPA under influence of environment and temperature at investigation of structural changes of HPA in 30% $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}/\text{SiO}_2$  and 30% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$  catalysts by TPR TPO, IR, and XRD methods at stages of their step-by-step reduction, subsequent oxidation at 773-1273 K and processing by water (298 K, superheated steam).

Obtained data indicate on lability of HPA/ $\text{SiO}_2$  system in oxidation-reduction conditions and influence of water at temperatures close to temperatures of the reaction of partial oxidation and oxidative dehydrogenation of alkanes and easy regeneration of active structure of HPC from finely divided mixture of oxides under influence of  $\text{O}_2$  and  $\text{H}_2\text{O}$ . It explains stability of the 12th series Mo HPC supported on Si-containing carrier at high temperatures (873-1073 K) at partial oxidative conversion of alkanes at the temperatures providing reversible destruction of HPA on oxides, dispersion the last under influence of  $\text{O}_2$  and formation of HPA under influence of water vapor and temperature at some preservation of HPA elements in samples.