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## Catalytic activity of selected heteropolyacids. Theory vs. experiment.

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Heteropolyacids (HPA) belong to a group of compounds, which due to their acid-base and redox properties catalyze the broad spectrum of reactions both homogeneous and heterogeneous. This is due to their specific properties, among which versatility of electronic and geometry structures, chemical compositions, reaction performance, thermal stabilities and stabilities in solutions are worth to be mentioned. The structure of HPA allows for many different modifications of primary, secondary and tertiary structures providing an opportunity to tailor their catalytic properties.

Systems, in which one of addenda atom is substituted by transition cation, are successfully used in reactions of selective oxidation of saturated and unsaturated, chain and cyclic hydrocarbons, where the presence of reactive oxygen species (ROS) such as singlet oxygen  $O_{2(1)}$ , superoxoions  $O_{2(1)}^{sup-}$ , hydroxo or hydroperoxoradicals (respectively  $HO\cdot$  or  $HOO\cdot$ ) are required. On the other hand HPA salts are used in reactions where acidic properties of catalysts are of primary importance.

Oxidation properties of heteropolyacids are studied as a function of: different transition metal or addenda atoms incorporated to the system, various forms of oxygen species adsorbed on the system, different solvents. In parallel, different mechanisms proposed for the generation of acidity in totally exchanged 12-tungsto- and 12-molybdo-phosphoric acid containing  $Al^{3+}$ ,  $Ga^{3+}$  and  $In^{3+}$  as counter-cations are discussed. As a test reaction ethanol conversion is considered. DFT methods are used to study atomic charges, bond orders, energy and character of frontier orbitals, density of states. Theoretical results are confronted against experimental ones.

Incorporation of transition metal in the structure of Keggin anions influences acidic/base character of active centers, characters of frontier orbitals as well as energy of interaction with substrates, changes are of local character. Changes of energetics of frontier orbitals are larger in case of HPW than in HPMo. As the results of TM incorporation to Keggin structure additional new peaks 3d TM characters arrive, located between valence and conduction bands.

Interaction of TM ions with oxygen species depends on chemical character of TM, solvent, geometric environment and substrate character. HPA systems modified by TM interacts with solvent molecule that becomes a sixth ligand. Here, exchange of ligands is energetically more favorable in case of PTMMo than in PTMW. Adsorption of  $O_2$  leads to the formation of single TM-OO bonds, the  $O_2$  molecule becomes activated. The effect is similar for both of PTMMo and PTMW.

Results of combined theoretical and experimental approaches show that  $MPW_{12}O_{40}$  and  $MPMo_{12}O_{40}$ ,  $M = Al^{3+}$ ,  $Ga^{3+}$ ,  $In^{3+}$  exhibit weak redox properties only for MPMo (small amount of acetaldehyde that is redox product is formed) or none for MPW salts. All tested salts exhibit strong acidic properties (i.e. the diethyl ether and ethylene) and the amount of both products strongly depends on chemical character of counter-cations and chemical character of addenda atoms in Keggin anions. The catalytic activities of MPMo/MPW salts is found to change in the following way:  $HPW > GaPW > InPW > AIPW \gg HPMo > GaPMo > InPMo > AIPMo$ .

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