

## **OxFA-processing of renewable plant and microbial biomass in the presence of solid heteropoly acid catalysts for the production of formic acid as hydrogen precursor**

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The significant negative impact on the environment and human health caused by the intensive use in industry and energy of traditional, gradually depleting fossil hydrocarbons makes it inevitable to search for alternative renewable sources of raw materials for industry and energy, as well as new approaches to their processing. Plant and microbial biomass seems to be one of the most promising sources of such raw materials for obtaining valuable chemical compounds for energy applications. Formic acid is one of the most perspective compounds which can be derived from biomass and involved into energy industry [1, 2, 3].

Formic acid is attracting more and more attention as a promising source of hydrogen (53 g H<sub>2</sub> per liter of formic acid). The main advantage of formic acid over molecular hydrogen is the simplicity and safety of its storage and transportation. Nowadays, new methods have already been proposed for replacing molecular hydrogen with formic acid in biofuel production processes.

According to the literature, the OxFA-process appears to be the most promising method for obtaining formic acid from plant and microbial biomass. Hydrolysis-oxidation of alternative feedstocks with molecular oxygen can be effectively carried out in the presence of bifunctional heteropolyacid catalysts (HPA), for example, H<sub>3+x</sub>PMo<sub>12-x</sub>V<sub>x</sub>O<sub>40</sub> (where x = 1, 2, 5) [1, 2, 3]. Bifunctional HPA catalysts appear to be highly promising because of their high Bronsted acidity and high oxidation potential. In addition, HPA belong to catalytic systems that meet the principles of "green chemistry". Currently, the yield of the target formic acid compound derived via OxFA-processing of plant and/or microbial biomass can reach 85%.

Traditionally, OxFA-transformation of biomass into formic acid is carried out in the presence of homogeneous HPA catalysts. It has been shown the possibility of formic acid synthesis from cellulose at the 66% yield in the presence of a Co<sub>0.6</sub>H<sub>3.8</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> solution in pure water without any additives [1].

An essential disadvantage of soluble HPA is the difficult separation of the catalyst from the reaction mixture and/or the main product. The problem may be solved using solid (heterogeneous) catalysts based on vanadium-containing heteropoly acids. Thus, application of cesium salts of HPA makes possible the production of formic acid with the yield equal to 51 % [2]. 30 % yields of formic acid can be achieved over organic tetrabutylammonium salt of HPA [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>3.5</sub>H<sub>0.5</sub>PMo<sub>11</sub>VO<sub>40</sub> from microalgae biomass [3]. High efficiency of heterogeneous HPA catalysts is shown in several cycles of the reaction [2, 3].

The present report will show our achievements in the field of development and application of heterogeneous HPA catalysts in biomass transformation to formic acid.

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### Literature:

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