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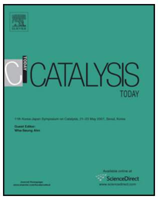

Hydrolytic oxidation of cellulose to formic acid in the presence of Mo-V-P heteropoly acid catalysts

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ABSTRACT

The reduction of oxygen-containing compounds, which is employed to produce biofuels from plant feedstock, requires a great amount of reductant that is commonly represented by molecular hydrogen obtained from non-renewable fossils. Formic acid can also serve as the reductant or hydrogen source in the production of such fuels. It is shown that formic acid can be obtained from mechanically activated microcrystalline cellulose with high yields (66%) by the one-pot catalytic process of hydrolytic oxidation in the presence of Mo-V-P heteropoly acids (HPA) possessing bifunctional (acidic and oxidizing) catalytic properties. Mechanical activation has a crucial influence on the cellulose reactivity and formic acid yields. The highest yield of formic acid was obtained by using the cellulose activated in a planetary mill, when its crystal structure was mainly crushed. The temperature of 150–160 °C and the oxidizing atmosphere (20% O_2 and 80% N_2) are found to be the optimal reaction conditions. Pressure was shown to exert no effect on the observable kinetics of the process. A search for the optimal HPA composition demonstrates that a maximum reaction rate is observed in the presence of HPA that provides the most acidic reaction medium. A linear dependence of the reaction rate on the concentration of H^+ ions and a more complicated dependence on vanadium content were revealed.

1. Introduction

The gradual depletion of fossil hydrocarbon sources has made it necessary to intensify a search for alternative renewable feedstocks for industry and energetics all over the world [1–11]. Plant biomass is among the most promising carbon-containing feedstocks for producing chemicals and fuels in future and a very high interest to biomass nowadays is aroused by the anxiety to substituted exhaustible fossil resources by renewable. Lignocellulosic biomass is the most abundant type of plant feedstocks not intended for the production of foodstuffs; it includes wastes from woodworking industry (offal timber) and wood-pulp mills (hemicellulose and lignin wastes), wastes from crop production and food industry (straw, maize core, seed husk and others), and finally the energy crops (Miscanthus, topinambour, millet, etc.) grown on wastelands.

Lignocellulosic biomass contains up to 60% of its major part—cellulose, the polymer of glucan. Being the cheapest and the most readily available polysaccharide in nature, cellulose is the most chemically resistant substrate out of all the biomass-derived carbohydrate feedstocks (e.g., inulin, glucose, xylan, etc.) due to its rigid crystalline structure and strong glycosidic bond between glucan units.

In this work we use of low-cost HPA catalysts for one-pot hydrolysis-oxidation of cellulose into formic acid. Heteropoly acids (HPA) are a large class of polyoxo compounds comprising the V and VI group metals [12]. The vast variety of HPA structures and properties has attracted attention of researchers from different fields. The solutions of Mo-V-phosphoric Keggin-type HPA-x and non-Keggin HPA-x' with high vanadium content and gross composition $H_aP_zMo_yV_{x'}O_b$ ($z > 1$; $x' > 4$) are the promising catalysts for various reactions because they possess not only the high Broensted acidity typical of all HPA groups, but also good oxidizing properties. The introduction of a specified number of vanadium atoms into such HPA and the partial substitution of H^+ ions by cations of other metals can be used to obtain the HPA solutions which properties

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are specific for a certain reaction type. In some works, HPA of this type were already employed as bifunctional catalysts [13,14]. In this connection, Mo-V-P HPA are considered to be the promising catalysts for hydrolytic oxidation of cellulose to formic acid.

Formic acid (FA) is a value-added chemical which is applied for production of medicaments, solvents, fragrances, and fibers, for conservation of food products and forage, and also used in pulp and leather industries [15]. Formic acid is a very promising substrate for synthesis of molecular hydrogen over metal catalysts [16–18]. Hydrogen is employed in industry in both “classic” fossil-based processes and new biomass-based manufactures, e.g., production of green diesel [1,19,20]. In future the increase in demand for hydrogen is expected as many strategies for biomass valorization into chemicals and fuels propose use of molecular hydrogen as a reagent, e.g., sorbitol and xylitol were included into the list of “platform molecules” [4,5]. Numerous novel processes suggested for production of liquid fuels [21–25] from lignocellulose require an external source of hydrogen. Interestingly, methods for the replacement of molecular hydrogen by formic acid by way of its in situ decomposition into CO_2 and H_2 to produce biofuel have been developed [26–32]. Therefore, the urgency for replacement the current fossil-dependent processes for production of formic acid and hydrogen by the renewable-based ones is well acknowledged. Formic acid might be synthesized as a side product of glucose acidic decomposition into levulinic acid [26,27,30–32] but the amount of formic acid thus produced is not sufficient to meet the anticipating demand for hydrogen. Carbohydrates might be converted into hydrogen via aqueous phase reforming, but the harsh process conditions (>200 °C) and the need for costly catalysts containing precious metals make such a process economically unfavorable [33].

The synthesis of formic acid from cellulose includes two sequential steps: the acid catalytic hydrolysis of cellulose to glucose and the subsequent oxidation of glucose to formic acid using an oxidant. The Mo-V-P HPA solutions, possessing both the acidic and oxidizing properties, are suggested as the promising bifunctional catalysts for the production of formic acid by the hydrolytic oxidation of natural polymers, such as cellulose and hemicellulose, under mild conditions [34–36]. HPA are known also as ‘green chemistry’ catalysts since they can be used in low-waste processes [37]. By now, we have found only three papers devoted to the synthesis of formic acid from biopolymers. The authors of References [35,36] compared the hydrolysis of cellulose, xylan hemicellulose, lignin, and real biological objects (pine, birch and poplar sawdust as well as blue-green algae) in the presence of HPA having the composition $H_5PV_2Mo_{10}O_{40}$. All the experiments were carried out at a low temperature, 90 °C, to prevent decomposition of the product at $T > 100$ °C. Cellulose was the most poorly hydrolyzable object, because a maximum yield of HCOOH with cellulose as a substrate was the lowest one among all other substrates and amounted to 7% for 24 h of the reaction [36]. Fu et al. [34] tested various vanadium-containing compounds, such as commercial HPA of the composition $H_5PV_2Mo_{10}O_{40}$, V_2O_5, $VOHPO_4$ and $VOSO_4$ in the oxidation of a model glucose substrate to reveal the most efficient oxidative catalyst. Mo-V-P HPA was found to be the most efficient catalyst for this process. The negative action of high oxygen concentrations and high temperatures on the target product yields was demonstrated. Overall, the authors [34] observed the highest yield of formic acid from cellulose equal to 35% at 100 °C in air at a pressure of 50 bar. The effect of HPA composition on the target product yields was not investigated in any of these works.

This work is aimed to study the effect of composition of a homogeneous heteropoly acid catalyst, its acidic and oxidizing properties on the overall kinetics and yields in the one-pot process of formic acid synthesis from cellulose for its further optimization. The heteropoly acid catalysts used in the study had different contents of vanadium and hydrogen atoms.

$$(1)\ V_2O_5 + H_2O_2(\text{cooled}) \longrightarrow VO(O_2) + \text{peroxo anions of } V^{5+} \longrightarrow H_6V_{10}O_{28}$$

$$(2)\ 1.4\ H_6V_{10}O^{28} + H_3PO_4 \longleftrightarrow H_9PV_{14}O_{42} + 1.2\ H_2O$$

$$(3)\ (12\text{-}x)\ MoO_3 + (1\text{-}x/14)\ H_3PO_4 + x/14\ H_9PV_{14}O_{42} + 2x/7\ H_2O \longrightarrow H_{3+x}PMo_{12\text{-}x}V_xO_{40}$$

Scheme 1. The overall scheme of the HPAs synthesis.

2. Experimental

2.1. Chemicals

Cellulose (fraction <0.10 mm, ZAO Vekton, St. Petersburg, Russia) and sulfuric acid (special purity, GOST 14262-76, Sigma Tech, Russia) were purchased. Milli-Q (Millipore, USA) water was used as a solvent in all the experiments.

2.2. Catalyst synthesis

An aqueous solution of HPA-x with the composition $H_5PMo_{10}V_2O_{40}$ (HPA-2) was obtained from stoichiometric amounts of V_2O_5, MoO_3, H_2O_2 and H_3PO_4 in two steps by the known technique [38,39]. At the first step, V_2O_5 was dissolved in a cold diluted H_2O_2 solution to form dark-red peroxo complexes of vanadium (V). Upon heating to room temperature, the resulting solution gradually decomposed with O_2 evolution to form ~0.0125 M of the orange solution of decavanadic acid $H_6V_{10}O_{28}$. The produced $H_6V_{10}O_{28}$ acid was immediately stabilized by adding an excess of H_3PO_4, which led to the formation of a dark-brown aqueous solution of $H_9PV_{14}O_{42}$ by Eqs. (1) + (2) from Scheme 1.

At the second step (Scheme 1, Eq. (3)), a freshly prepared aqueous solution of $H_9PV_{14}O_{42}$ was gradually introduced into the boiling suspension of $MoO_3 + H_3PO_4$. MoO_3 slowly dissolved under stirring of the resulting mixture to form a homogeneous HPA-x solution with a specified composition.

Aqueous HPA-x’ solutions of composition $H_{11}P_3Mo_{16}V_6O_{76}$ (HPA-6′) and $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10′) with a high vanadium content were prepared in a similar way, the additional amount of vanadium being stabilized by an excess of H_3PO_4 according to the technique described [40].

A solution of HPA-2 salt with the composition $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ (Co-HPA-2) was obtained by dissolution of cobalt carbonates in hot solutions of the produced salt.

2.3. Catalyst characterization

The composition of freshly prepared solutions was investigated by ^{51}V and ^{31}P NMR spectroscopy on a Bruker AVANCE 400 high-resolution NMR spectrometer using 85% H_3PO_4 and $VOCl_3$ as external standards. According to the acquired data, both the HPA-x and HPA-x’ solutions are complex equilibrium mixtures of a close composition. Such solutions contain the Keggin-type heteropoly anions with different number of vanadium atoms, H^+ ions, VO^{2+} cations, phosphoric acid, and possible products of their interaction with each other. Therewith, the number of lines corresponding to different HP anions increases with x (the number of vanadium atoms). A detailed description and images of the spectra for such solutions are given in our earlier studies of HPA-x and HPA-x’ [38–42].

2.4. Mechanical activation of cellulose

The study was conducted with pure cellulose for chromatography (fraction <0.10 μm, ZAO Vekton, St. Petersburg, Russia).

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