Hydrolysis of cellulose using heteropoly salts derivatives from $H_3PW_{12}O_{40}$ with different redox properties as catalysts

Ana Carolina Cunha Arantes[1], Anna Cláudia Santos de Oliveira[1],
Willian Miguel da Silva Borges[1], Maria Lucia Bianchi[1],
Eliane Cristina de Resende[2]

[1] Federal University of Lavras, Department of Chemistry, P.O. Box 3037, 37200-000, Lavras, MG, Brazil e-mail: anacarolinacarantes@gmail.com, annaclaudia_sam@hotmail.com ,will_msb@hotmail.com, bianchi@dqi.ufla.br
[2] Department of Science and Language, Federal Institute of Minas Gerais, 38900-000, Bambuí, MG, Brazil e-mail: eliane.resende@ifmg.edu.br

ABSTRACT

Heteropoly salts containing different numbers of vanadium atoms ($K_4[PVW_{11}O_{40}]$ - $KPWV_1$ and $K_6[PV_3W_9O_{40}]$ - $KPWV_3$) were synthesized from the heteropoly acid $H_3PW_{12}O_{40}$ (HPW), and used as catalysts in hydrolysis of cellulose reactions in order to change the redox properties and verify whether the cluster of catalysts are involved in mechanism reaction. The hydrolysis reactions following a full 23 factorial design with the variables: mass ratio (catalyst/substrate), reaction time and temperature. The variables evaluated were significant at a 90% confidence level including second and third order interactions. According to the conducted experiments, the catalysts were all active in hydrolysis. The best results occurred when HPW was used suggesting that the redox properties did not have much influence in depolymerization of cellulose and the hydrolysis mechanism are assigned to acidic properties of the medium. The main products obtained from the reactions were glucose and HMF, which are products of great interest in the chemical industry.

Keywords: hydroxymethylfurfural, redox properties, tungstophosphoric acid.

1. INTRODUTION

Heteropoly acids (HPAs) are used as catalysts in a wide variety of chemical reactions [1, 2, 3, 4]. They are included in a class of polyoxometalates which are defined as ionic clusters, with general formula $[M_mO_y]^{p-}$ or $[X_xM_mO_y]^{q-}$, where M is a transition metal (generally V, Mo or W), and X is a heteroatom (typically Si, B or P). When the counter ions of heteropoly anions are protons, they are called HPAs [5].

The HPAs have acidic and redox catalytic properties, are thermally stable, and show high solubility in water and organic solvents. These properties are dependent upon the metal and are not influenced substantially by the heteroatom. The most important HPAs in catalysis are the Keggin structure; among them, tungstophosphoric acid (HPW) is widely used [6].

The primary structure of polyoxometalates is a polyanion, a cluster with a central tetrahedron (XO_4) surrounded by twelve octahedra (MO_6). The secondary structure concerns the three-dimensional arrangement of the polyanion and counter ions. The tertiary structure represents how the secondary structure is grouped into solid particles and is responsible for pore volume, surface area, particle size and dispersion. Related to these factors, the tertiary structure exerts the largest influence on the catalytic activity of HPAs [7].

The HPAs can be used as catalysts in acid hydrolysis of cellulose [8, 9, 10, 11]. Cellulose is a major component of biomass, a renewable raw material for the production of ethanol and numerous additional chemical products [12]. The cellulose extracted from biomass is composed of D-glucose units linked by glycosidic bonds that when hydrolyzed, can release monomers of glucose, which are fermentable to produce ethanol [13]. First or second generation bioethanol can be used as a substitute for gasoline (a non-renewable resource) and provides environmental benefits, like less greenhouse gases released into the atmosphere [14].

Besides the production of glucose monomers by hydrolysis, other interesting products can be synthesized by dehydration of glucose and cellulose. One of these is hydroxymethylfurfural (HMF), which is classified by the U.S. Department of Energy as one of the ten most important molecules based on a platform chem-

ical derived from biorefineries [15].

From HMF, several molecules can be produced. These molecules are the result of different catalytic routes when temperature, time, reaction medium, pH, catalysts, etc. are varied [16]. The use of HPAs for the production of HMF has been previously reported. [17, 18, 19]. The reaction mechanism proposed to hydrolysis of cellulose using HPAs is the same as using mineral acids, starting with protonation of glycosidic oxygen and cleavage of C1-O linkage. The nucleophilic attack of water on C1 with acid regeneration finishes the process. Considering this mechanism, the cluster of HPA does not affect the process. However, a previous work [20] showed that during aerobic oxidation of cellulose in presence of $[PMo_{12-n}VnO_{40}]^{(3+n)-}$ heteropoly anions in aqueous medium, the cellulose oxidative depolymerization was mainly associated with redox properties through the action of the VO_2^+ ions, released from heteropoly anions via partial dissociation under acidic conditions.

In this context, the purpose of this work was evaluate the influence on mechanism of hydrolysis reaction. Were verify whether the reaction occurs only by the presence of the hydrogen in the middle, or if mechanisms redox are involved. For this, modifications have been made in the redox properties of heteropoly salts (synthesized from HPW) replacing W atoms by V atoms [1]. The heteropoly salts synthesized ($K_4[PVW_{11}O_{40}]$ ($KPWV_1$) and $K_6[PV_3W_9O_{40}]$ ($KPWV_3$)) they also were characterized and applied as catalysts for the cellulose hydrolysis reaction.

2. MATERIALS E METHODS

2.1 Synthesis and characterization of catalysts

HPW (Fluka) was used in reactions and as the synthetic precursor of heteropoly salts. The heteropoly salts, $KPWV_1$ and $KPWV_3$ were synthesized following methodology described by Domaille [20]. For $KPWV_1$, a solutions of HPW and $NaVO_3$ (Vetec) were mixed and the salt was precipitated using KCl (Vetec). For $KPWV_3$, the $NaVO_3$ was added to a buffer solution of acetic acid/sodium acetate, followed by addition of $Na_8H[PW_9O_{34}]$ (synthesized from methodology described by Massart [21]. The salt was also precipitated by adding KCl. The heteropoly salts were analyzed by FTIR in an IR Affinity equipment using KBr pellets; energy dispersive X-ray (EDS) in a scanning electron microscope (SEM) device coupled with EDS/INCA 350; and a nuclear magnetic resonance (NMR) spectrometer with a 105.19 MHz 51V probe. NMR samples were dissolved in deuterated water (D_2O) and filtered before acquisition.

2.2 Hydrolysis reactions

The hydrolysis reactions were performed in a closed system, following a full 23 factorial design with the variables: mass ratio (catalyst/substrate), reaction time and temperature. The factorial design, described in Table 1, was analyzed using Chemoface® software (version 1.4) and adjusted according to the experimental conditions found. Microcrystalline cellulose (Synth) was used as substrate. The catalysts used were HPW, $KPWV_1$ and $KPWV_3$. The reaction products were analyzed using a Shimadzu UV-1800 UV/Vis spectropho-tometer and the total reducing sugar content (%TRS) was quantified by dinitrosalicylic acid method (DNS) [22] at 540 nm. Analyses by high performance liquid chromatography (HPLC) were conducted on a Shimadzu Prominence chromatograph equipped with a RID-10A detector, a LC-20AT pump and a Shim-pack Amino-

Na column (6 mm × 100 mm; 5 mm particle size) maintained at 80 °C. The isocratic injection used water as mobile phase and an injection volume of 20 μL on a flow of 0.4 mL.min^{-1}. In both analyses, glucose (Merck) was used as a reference standard. In order to identify additional products, the reaction mixtures were analyzed utilizing mass spectrometry with electrospray ionization (Agilent-1100 ESI-MS). The products were analyzed by direct infusion with a flow injection 15 μL min^{-1}. The injection conditions were: 320 °C, 3.5 kV capillary voltage and mass adjusted to 300 and ICC 30000 with an accumulation time of 300 ms. Nitrogen was used as drying gas at a flow rate of 6 L min^{-1}. For ESI-MS/MS, the ion of interest was isolated by electron capture in an ion trap and excited by collision induced dissociation (CID) using helium.

Table 1: Full factorial experimental design of hydrolysis reactions.

| LIMITS	VARIABLE		
	MASS RATIO (CATALYST/ SUBSTRATE)	TIME (h)	TEMPERATURE (°C)
Lower limit (-)	0,33	2	100
Central Point (0)	1,66	4	125
Upper limit (+) Experiment	3,00	6	150
1	-	-	-
2	-	-	+
3	-	+	-
4	-	+	+
5	+	-	-
6	+	-	+
7	+	+	-
8	+	+	+
Central Point	0	0	0

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of catalysts

The heteropoly salts were synthesized by replacing tungsten atoms from HPW with vanadium atoms; they were then characterized to verify structural similarities and differences relative to HPW. FTIR spectroscopy is widely used for the characterization of HPAs in view of the Keggin anion demonstrates characteristic bands in the region between 700-1200 cm^{-1} [4], these bands correspond to four types of oxygen atoms in the structure. Furthermore, FTIR in this region can be used to verify preservation of the primary structure in the synthesized heteropoly salts [24], Figure 1 displays the FTIR spectra for HPW, KPWV$_1$ and KPWV$_3$. The presence of characteristic peaks of the Keggin structure can be observed: at 798 cm^{-1}, stretching of W–O–W on the edges; at 890 cm^{-1}, W–O–W stretching at the vertices; at 983 cm^{-1}, the asymmetric W–O stretching with terminal oxygen atoms; and at 1080 cm^{-1}, asymmetrical P–O stretching. In addition, a band corresponding to the water hydration ion ($H_5O_2^+$) in the secondary structure is observed at 1620 cm^{-1} [24]. The similarity of the spectra verifies that the primary structure of HPW was maintained in the synthesized heteropoly salts (KPWV$_1$ and KPWV$_3$).
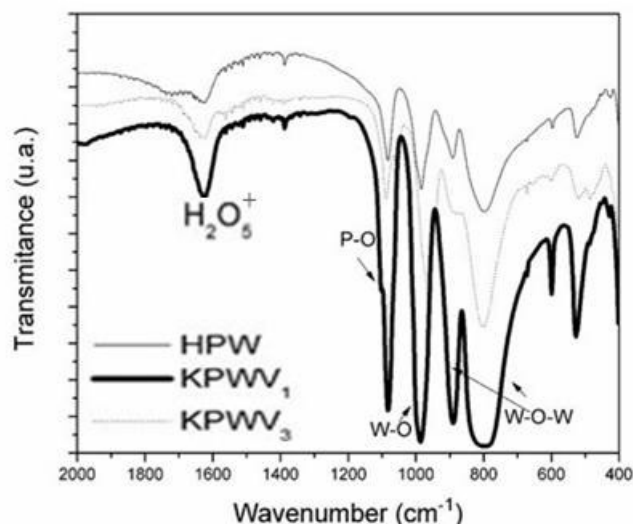
Figure 1: FTIR spectra of catalysts - HPW, $KPWV_1$ and $KPWV_3$.

EDS is a semi-quantitative analysis of elements present on the sample surface and identification occurs through specific energy emissions of each element. An area was delimited from the scanning electron microscopy (SEM) images generated and the elements within this area were quantified by EDS. In the analysis of HPW (Figure 2a), the main elements present are phosphorus, tungsten and oxygen. For $KPWV_1$ (Figure 2b) and $KPWV_3$ (Figure 2c), the incorporation of vanadium can be observed in each spectrum, with the data for $KPWV_3$ demonstrating a larger quantity of vanadium. In addition, potassium and chlorine remaining from the synthesis [21] and elements from the HPW precursor are also present.
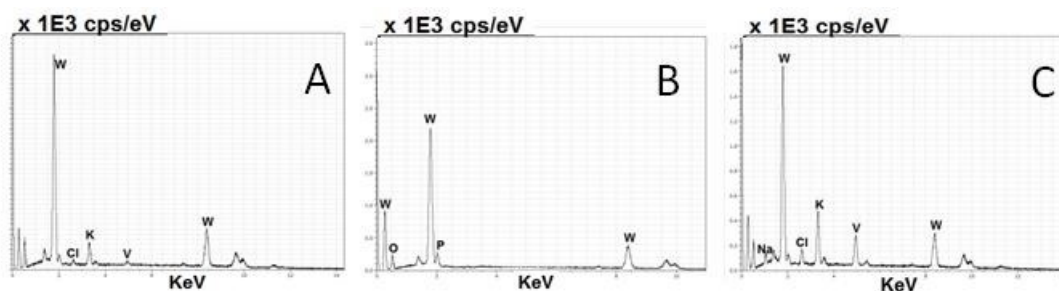
Figure 2: EDS spectrum of catalysts a) HPW, b) $KPWV_1$ and c) $KPWV_3$

NMR spectroscopy is an important tool for characterization of heteropoly compounds [5] and the ^{51}V NMR can provide information about the presence of vanadium in the structure. Figure 3 illustrates the NMR spectra for HPW, $KPWV_1$ and $KPWV_3$. The HPW spectrum indicates no signal because it does not have vanadium in the structure. In $KPWV_1$ there is one signal, signifying incorporation of a single vanadium atom in the structure (it is assumes that incorporation of a second vanadium atom will probably occur in a different chemical environment to the first and result in two peaks in the NMR spectrum). In $KPWV_3$, the presence of more than one vanadium atoms can be confirmed due to the presence of more than one signal. Although, the NMR spectrum cannot confirm the presence of three vanadium atoms, the broad upfield peak indicates the possibility that two vanadium atoms are in symmetrical positions in the structure. These symmetrical positions were described by Domaille [21]. and one possibility is shown in the structures in Figure 3.
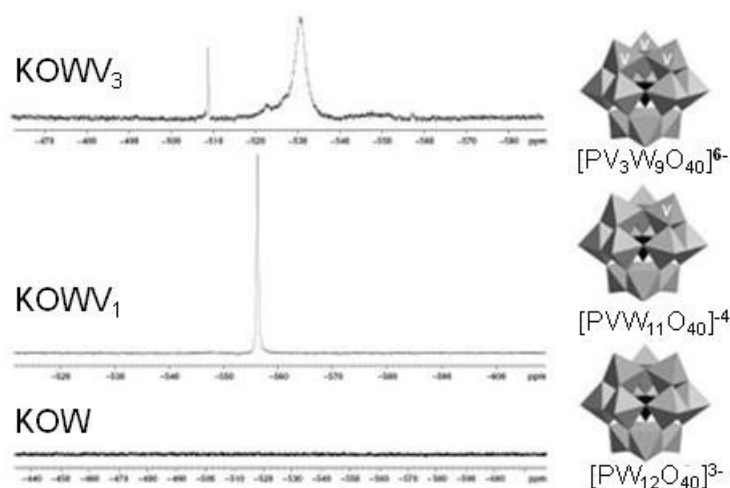
Figura 3: 51V NMR spectra and possible positions of the V atoms (adapted from Mizuno and Kamata, 2011) in the structures of catalysts - HPW, KPWV$_1$ and KPWV$_3$
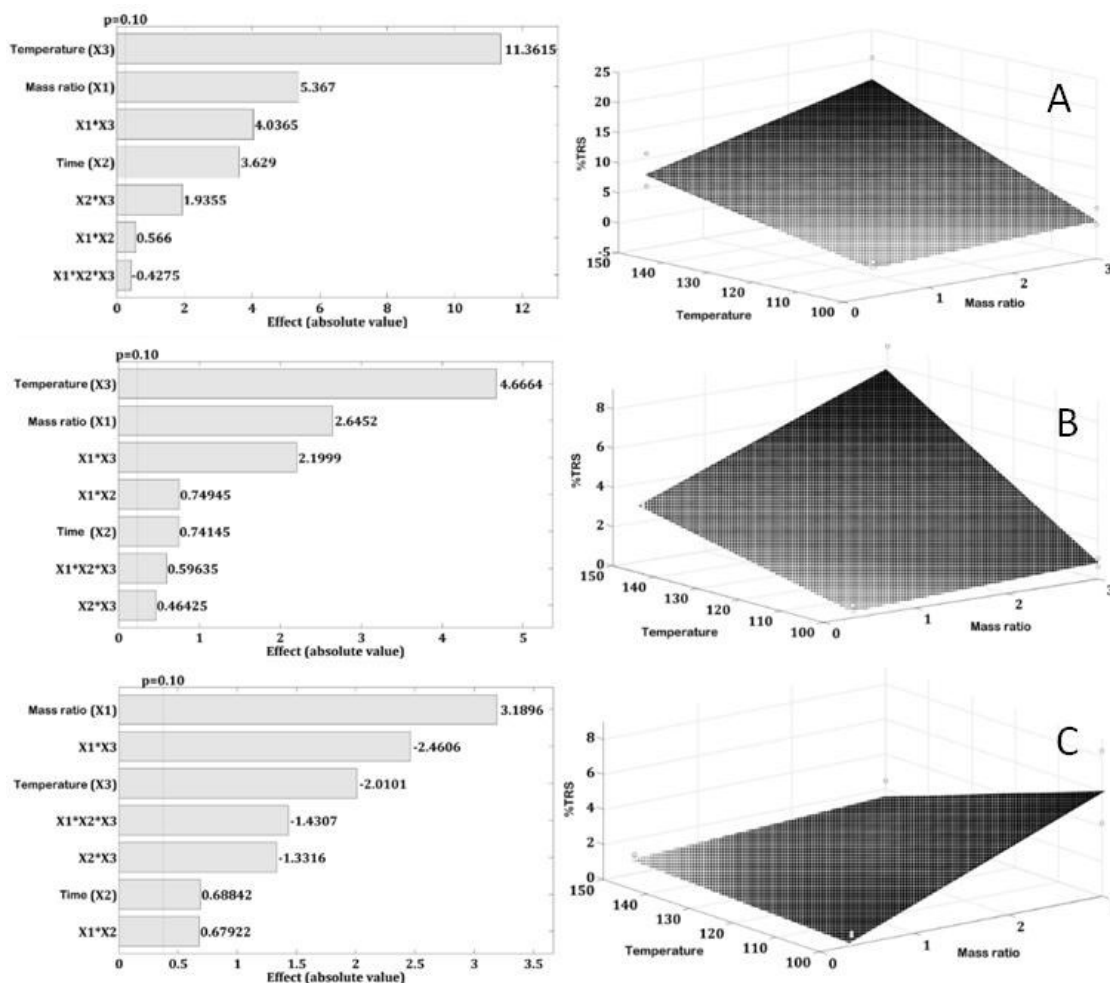
3.2 Hydrolysis reactions

The cellulose hydrolysis reactions followed the experimental design shown in Table 1. The factorial design allows for evaluation of several variables in a reduced number of experiments. The variables and levels defined in a factorial design depend on the system and the reaction medium [26]. The variables evaluated (mass ratio catalyst/substrate, reaction time and temperature) were significant at a 90% confidence level and included second and third order interactions, as shown in Pareto's chart (Figure 4a) using cellulose as the substrate and HPW as the catalyst.

In a first order analysis, the temperature has greater influence than the mass ratio and the time on %TRS results. The second and third order interactions are significant, however, less so than temperature and mass ratio. Since the time variable has smaller influence on the results, the response surface (Figure 4a) was plotted considering the time at level 0 (4 hours) and showing mass ratio, %TRS and temperature on the X, Y and Z axes, respectively.

The response surface demonstrates that the best reaction results occur at maximum levels of factorial design; in other words, when the temperature and amount of catalyst used is high, the conversion of %TRS is also high. In a second analysis, longer time periods were also shown to promote higher conversion. This trend is also observed when using KPWV$_1$ as the catalyst, and can be observed in Pareto's chart and in the response surface (Figure 4b).

Although the trend of the first order variables are the same, there is a large decrease in conversion of %TRS when using the KPWV$_1$ catalyst. This reduction also occurs with KPWV$_3$, and can be observed in the response surface (Figure 4c). The results obtained from the %TRS with KPWV$_3$ are smaller than those with KPWV$_1$; they also display a different conversion trend, as shown in the Pareto chart (Figure 4c). The best results were obtained at lower temperatures, but the mass ratio trend remained constant, where greater catalyst quantity resulted in higher conversion of %TRS.

Figura 4: Pareto's chart and response surface from factorial design of hydrolysis reactions using cellulose as substrate and a) HPW, b) KPWV$_1$, c) KPWV$_3$ as catalyst. The reactions were performed in a closed system, following a full facto-rial design 23, analyzed using Chemoface®, with confidence level 90% and the varia-bles: mass ratio (catalyst/substrate) (lower limit 0.33 and upper limit 3.00), reaction time (lower limit 2h and upper limit 6h) and temperature (lower limit 100 °C and upper limit 150 °C).

The decrease in %TRS conversion can be explained by the acidity of the catalysts, where the HPW was the most acidic of those used [1]. This was confirmed by measuring the pH of the reaction media; the HPW medium was found to be pH 2.5, while KPWV$_1$ was pH 3.7, and KPWV$_3$ was pH 7.2. Replacing W atoms with V atoms in the structure was intended to change the redox properties of the heteropoly anion and verify whether the mechanism of the hydrolysis reaction occurs only by the presence of the hydrogen in the middle, or if there was some characteristic of the heteropoly anion involved. Due to the significant decrease in acidity, were performed additional reactions using the acids of the heteropoly salts HPWV$_1$ (H$_4$[PVW$_{11}$O$_{40}$]) and HPWV$_3$ (H$_6$[PV$_3$W$_9$O$_{40}$]) at central point conditions.

At the same pH (2.5), it is clear that acidity of the medium is the main factor in hydrolysis of cellulose comparing the results in %TRS reactions using HPW (4.1%), HPWV$_1$ (2.2%) and HPWV$_3$ (1.1%). Although a redox reaction occur promoted by VO$_2^+$ ions, observed in color changes, the depolymerization cannot be associated with that, because these reactions require an oxidizing reactant to continuous the cycle, like O$_2$ or H$_2$O$_2$ [20].

Analyses to quantify %TRS measures all sugars, including glucose, which is a product of interest [23]. In order to determine if there was glucose formation, analyses were performed by HPLC and the yields of glucose from the reactions with different catalysts are shown in Table 2.

Table 2: Glucose yields using factorial design and different catalysts

EXPERIMENT	YIELDS OF GLUCOSE (%)		
	HPW	KPWV$_1$	KPWV$_3$
1	0.05	0.00	0.05
2	1.85	1.34	0.09
3	0.26	0.00	0.05
4	12.98	1.44	0.03
5	0.88	0.00	0.00
6	12.71	7.24	0.10
7	18.76	0.00	0.00
8	37.95	8.23	0.05
Central Point	4.68	1.45	0.03

Low conversion to glucose can be observed, particularly when using heteropoly salts. However, in addition to glucose, there was formation of another compound in larger quantities; this compound was identified, by mass spectrometry, as HMF, an important molecule in chemistry industry. The analysis was performed on the products of the hydrolysis reaction corresponding to the central point of the factorial design using HPW as the catalyst.

Among the peaks, could be observed the presence of the signal corresponding to HMF at m/z = 127. This compound was isolated and the fragments at m/z = 98 and 108, could be observed in the MS/MS spectrum, relates to loss of CO and loss of water, respectively. According to the above analyses, HPW, KPWV$_1$ and KPWV$_3$ present themselves as good catalysts for the production of HMF, precursor of several different molecules.

4. CONCLUSION

The heteropoly salts were synthesized from HPW and the characterizations showed the effectiveness of the synthesis. The catalysts were all active for the production of glucose and HMF. Although the hydrolysis occurred when the heteropoly salts were used, a large decrease in %TRS conversion was observed (compared to HPW); this was a result of the difference in acidity between the catalysts, showing that cluster of HPA is not involved in reaction mechanism.

5. ACKNOWLEDGEMENTS

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