



Oxidation of cyclohexanol to epsilon-caprolactone with aqueous hydrogen peroxide on $H_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

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ABSTRACT

Liquid phase cyclohexanol catalytic oxidation to cyclohexanone and epsilon(ϵ)-caprolactone were studied using aqueous hydrogen peroxide as oxidant and $H_3PW_{12}O_{40}$ (HPA) and $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ (Cs-salt) as catalysts. The hydrophobic and insoluble Cs-salt showed the highest activity (per unit catalytic weight and turnover number) and selectivity to (ϵ)-caprolactone. The ultrafine Cs-salt crystallites could be filtered and recycled. Solvent effects on the activity and selectivity and the rate of peroxide decomposition were assessed and they were correlated to their polarity and protic/aprotic nature. When employing acetonitrile at 90 °C the highest activity and selectivity were achieved and also the lowest rate of hydrogen peroxide decomposition.

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1. Introduction

In recent years, the development of liquid phase processes has been accelerated because of certain advantages, associated especially with liquid phase oxidation. Such advantages are higher yield, improved selectivity and milder reaction conditions.

Furthermore heteropoly acids (HPAs) have proved to be an alternative to traditional acid catalysts, such as sulfuric acid and aluminum chloride, due to their strong acidity and their null environmental impact. However the use of pure HPA catalysts is hampered by their low surface area and high solubility in polar reaction media. The latter produce problems during separation. These problems can be overcome by partially exchanging protons of the parent HPA with large cations, such as Cs^+ , K^+ , Rb^+ and NH_4^+ , which are more water-insoluble and have a rather high surface area (exceeding $100\text{ m}^2\text{ g}^{-1}$). The so called heteropoly compounds (HPCs), including the HPA salts, have been intensively studied as acid and oxidation catalysts for both heterogeneous and homogeneous processes due to their unique acid and redox properties [1,2].

Hydration of propylene in the liquid phase and oxidation of methacrolein or isobutyric acid to methacrylic acid are two examples of industrial processes [3]. Insoluble HPCs derived from $H_3PW_{12}O_{40}$ by substitution of one to three hydrogen atoms for monovalent cations (K^+ , Cs^+ , Rb^+ , NH_4^+) were used in the oxidation of acrolein [4]. It has been reported that HPCs are not good cata-

lysts for liquid phase oxidations because their reoxidation by dioxygen is rather slow [5]. However they efficiently catalyze the oxidation by hydrogen peroxide [6]. Also their use as co-catalysts for Wacker oxidation has been extensively investigated [7]. Catalytic liquid phase alcohol oxidation is a research area on active development due to the increasing need to substitute conventional stoichiometric oxidizing agents, such as nitric acid, organic peroxides and metal oxides, with environmentally benign oxidants such as air, molecular oxygen or hydrogen peroxide. A variety of metal compounds have been investigated including molybdenum, tungsten, ruthenium and copper complexes [8].

In this contribution we report an interesting alternative for the production of cyclohexanone from cyclohexanol using a tungstophosphoric acid and a recyclable cesium salt of that heteropoly acid as depicted in Fig. 1.

2. Experimental

2.1. Materials

The reagents $H_3PW_{12}O_{40}$ (Merck), cyclohexanol (Vetec, 99%), acetonitrile (Tedia, 99.9%), methanol (Tedia, 99.9%), tetrahydrofuran (Tedia, 99.8%), 2-butanol (QM, 99.5%) and acetone (QM, 99.5%) were used as purchased. The aqueous 70 wt% hydrogen peroxide was supplied by Peróxidos do Brasil. The cesium salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared by precipitating an appropriate amount of Cs_2CO_3 (Sigma) solution by addition of an aqueous solution of the HPA.

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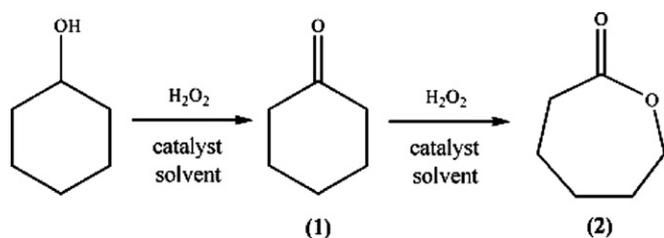


Fig. 1. Equation representing the cyclohexanol oxidation to cyclohexanone (1). The subsequent cyclohexanone oxidation produces epsilon (ϵ)-caprolactone (2).

2.2. Characterization of catalyst

- The textural properties of the solid (specific surface area, pore volume and pore size distribution) were measured in a Quantachrome NOVA-1000 sorptometer by physisorption of N₂ at the temperature of -196.5 °C.
- The catalysts were characterized by X-ray diffraction of powder samples in a Shimadzu XD-3A spectrometer, using CuK α radiation, with a step of 0.02° and a counting interval of 1 s.
- Dehydration of 1-4-butanediol in liquid phase was employed as a means of assessing the acidity of the catalyst [9]. The reaction was carried out in a Parr autoclave. Typically, 1.8 g of 1-4-butanediol, 12 mL of dioxane (solvent) and 0.12 g of the catalyst were charged to the reactor. The mixture was heated to 100 °C under vigorous stirring to start the reaction. The products of the reaction were analyzed by gas chromatography, using calibration curves and di-*n*-butyl-ether (10 mmol) as internal standard.
- Acid site densities were determined by temperature programmed desorption (TPD) of NH₃ preadsorbed at 100 °C. Samples (200 mg) were treated in He at 300 °C for 0.5 h and then exposed to a (1%) NH₃:He stream for 40 min at 100 °C. Weakly adsorbed NH₃ was removed by flowing He at 100 °C during 2 h. The temperature was then increased at a rate of 10 °C min⁻¹ and the evolved NH₃ in the effluent was measured by a thermal conductivity detector.

2.3. Catalytic experiments

The oxidation of cyclohexanol was carried out either in a stainless steel reactor or in a three-necked round bottom glass flask immersed in an oil bath equipped with a thermometer and a magnetic stirrer. Typically, 10 mmol of cyclohexanol and 40 mmols of aqueous hydrogen peroxide were first dissolved in 5 g of solvent and loaded to the reactor. Then 0.12 g of the catalyst were added and the stirring rate and the temperature were adjusted. The reaction was carried out for the indicated desired time. Then the reaction mixture was filtered, diluted with methanol and analyzed by gas chromatography using an HP 5890 gas chromatograph equipped with an AT-WAX capillary column (60 m \times 0.25 mm \times 0.25 m) and a FID detector. For the chromatographic separation the following temperature programme was used: 3 min at 40 °C; 20 °C min⁻¹ up to 150 °C; 2 min at 150 °C; 25 °C min⁻¹ up to 260 °C and 10 min at 260 °C. The products were quantitatively determined using calibration curves obtained with standard solutions of cyclohexanone and ϵ -caprolactone.

2.4. Hydrogen peroxide measurement

Hydrogen peroxide in the reaction medium was determined according to Ref. [10]. Fifty microliter of an aqueous 25 wt% acetic acid solution and ca. 20 g of dry ice for deaeration were added to an

Erlenmeyer. After a few minutes 2.0 g of potassium iodide (Synth, p.a.) and 3 drops of a 1 wt% ammonium molybdate (Vetec, p.a.) solution were added. To this mixture 200 μ L aliquots of the reaction mixture were added and then a titration with sodium thiosulfate (0.1 mol L⁻¹) was performed. The end point was detected by the disappearance of the dark blue color and the formation of a clear colorless solution.

3. Results and discussion

3.1. Catalyst characterization results

The surface areas of the HPA and its Cs-salt after being treated at 300 °C were 6 and 45 m² g⁻¹, respectively (Table 1). The powder X-ray diffractograms of the Cs-salt and the free acid were similar with only a small variation in the peaks intensities, thus confirming the retention of the Keggin structure in the Cs-salt after calcining at 300 °C.

The acidic properties of the solids were studied by means of the reaction of 1-4-butanediol dehydration at 100 °C. After 4 h reaction only tetrahydrofuran (THF) was observed as a product. The NH₃ TPD results showed that HPA and its cesium salt had very strong acid sites. These are responsible for their high activity in the liquid or gas phase reaction as reported elsewhere. It has been demonstrated that HPA and its Cs-salt possesses superacidity, with a H₀ value of ca. -13.6 . It has been found that gamma-alumina (commercial sample supplied by Across) needed a reaction temperature of 210 °C in order to show a comparable catalytic activity as HPA or its Cs-salt at 100 °C [11,12]. Activity values at 4 h reaction time are summarized in Table 2. The results obtained with a strong acid functionalized polymeric catalysts (Amberlyst 15, Rohm and Haas) is also included.

3.2. Catalytic oxidation

3.2.1. Influence of the catalyst

In order to develop a new catalytic process using a solid heteropoly compound the acidity and oxidizing power can be separately and conveniently controlled by changing the constituting elements. Redox potential of HPA is known to be controlled by the

Table 1
Catalysts properties

Catalyst	Surface area m ² g ⁻¹	Average pore diameter (Å)	Acid amount mmoles g NH ₃	% 1-4-butanediol conversion (4 h)
HPA	6	–	0.316	55
Cs-salt	145	71	0.065	17
Amberlyst 15	45 ^a	240 ^a	4.8 ^a	60
Alumina	280	–	–	not observed

^a Technical description of Rohm and Haas.

Table 2
Solvent effect on the cyclohexanol oxidation

Solvent	Dielectric constant	Cyclohexanol conversion (%)	Selectivity (%)		H ₂ O ₂ consumption (%)
			Cyclohexanone	ϵ -caprolactone	
ACN	37.5	56	89	11	60
Acetone	20.7	15	76	24	75
THF	7.58	13	100	–	62
Methanol	32.7	14	100	–	100
2-Butanol	10.9	36	89	11	100

Catalyst = Cs_{2.5}H_{0.5}PW₁₂O₄₀: 120 mg, cyclohexanol: 10 mmol, H₂O₂ (70 wt%): 40 mmol, solvent: 5 g, t: 4 h, T: 90 °C.

valence of the central atom. However alkaline earth metals which are not reducible can also replace the balancing protons to give partially substituted salts of the heteropoly acids leading to modified acidity and thermal stability while retaining unaltered the redox properties.

Figs. 2 and 3 show the percentage conversion (mol %) of cyclohexanol as a function of the reaction time using acetonitrile as solvent and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as catalysts. Both catalysts exhibited good activity and a high selectivity to cyclohexanone. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ exhibited a higher cyclohexanol conversion than $\text{H}_3\text{PW}_{12}\text{O}_{40}$. At 6 h of reaction time the Cs-salt converted 90% (mol basis) of the cyclohexanol and the HPA only 60%. After 14 h the conversion with HPA did not reach more than 70%.

The turnover number (TON) of the reaction was also calculated. TON is defined as the number of reacted cyclohexanol molecules divided by the number of protons in the catalysts. The TONs at 6 h for the Cs-salt and HPA were 500 and 55, respectively. For the Cs-salt we used the total amount of protons in the bulk calculated from the chemical composition (0.15 mmol g^{-1}). For HPA the

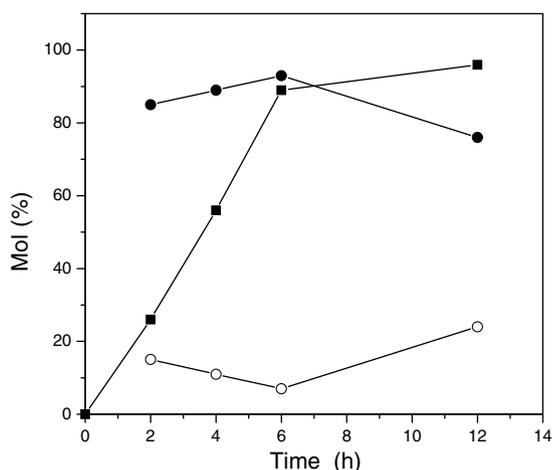


Fig. 2. Cyclohexanol oxidation as a function of reaction time using $\text{H}_{0.5}\text{Cs}_{2.5}\text{PW}_{12}\text{O}_{40}$ as catalyst. Cyclohexanol conversion (■), cyclohexanone selectivity (●), ϵ -caprolactone selectivity (○). Catalyst: 120 mg; cyclohexanol: 10 mmol, H_2O_2 (70 wt%): 40 mmol, solvent: 5 g acetonitrile, T : 90°C .

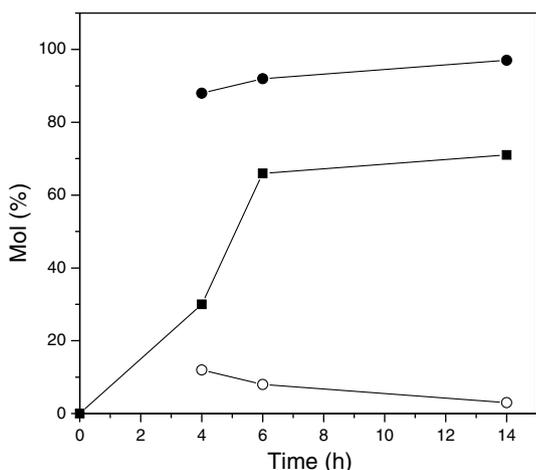


Fig. 3. Cyclohexanol oxidation as a function of reaction time using $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as catalyst. Cyclohexanol conversion (■), cyclohexanone selectivity (●), ϵ -caprolactone selectivity (○). Catalyst: 120 mg, cyclohexanol: 10 mmol, aqueous H_2O_2 (70 wt%): 40 mmol, solvent: 5 g acetonitrile; T : 90°C .

amount of protons was calculated from the composition assuming an average formula of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 18\text{H}_2\text{O}$ (0.96 mmol g^{-1}) [13]. Both catalysts used have been reported to have superacidity [14]. The higher catalytic activity of the Cs-salt is related to its acidity and structure. This catalyst is reported to have an enhanced water tolerance [15]. Generally solid acids are severely poisoned by water and they usually lose their catalytic activities in aqueous solution affecting both the catalyst performance and the reaction equilibrium.

Although $\text{H}_3\text{PW}_{12}\text{O}_{40}$ has a higher acid strength its Cs-salt has a higher surface acid site population. It is important to mention that the population of very strong acid sites in these solids is only a small fraction of all protons available. Some authors have already pointed out this ambiguous acid behavior [16]. The exposure of protons is markedly dependent on the surface area for these heteropoly compounds. The presence of micropores and mesopores on $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ [17] probably makes it easier to the substrate to access all protons in the structure, thus making this compound more effective than $\text{H}_3\text{PW}_{12}\text{O}_{40}$. With the presence of larger pores in its structure and a higher surface area $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ has more surface protons available for the catalytic reaction. In contrast, reactant molecules would have more problems in reaching the internal protons of the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ lattice.

3.2.2. Solvent influence

The dependence of the conversion of cyclohexanol, the selectivity and the extent of the decomposition of hydrogen peroxide on the kind of solvent was studied using $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ as catalyst. Table 2 shows the characteristics of the different solvents used and their protic/aprotic nature. These solvents were chosen because they form a single phase with the organic substrate and the hydrogen peroxide. It could be noted that the conversion increased with the polarity of the aprotic solvent, while an opposite behavior was observed for the protic ones. Acetonitrile (ACN), the most polar aprotic solvent, had the best performance. When compared to methanol, that has a similar polarity but is protic, it can be seen that acetonitrile yields twice the conversion. In the case of the aprotic solvents cyclohexanol competes only with water for adsorption on the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ surface. In the case of protic solvents, besides that competition, the substrate additionally competes with the solvent for adsorption on the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ surface thus decreasing the overall activity.

Data on hydrogen peroxide decomposition are also shown in Table 2. It can be seen that the decomposition is influenced by the kind of solvent used. Decomposition was higher when using protic solvents. An explanation for this behavior could involve the hydrogen peroxide decomposition mechanism [18]. In a protic solvent the decomposition of hydrogen peroxide proceeds by a chain-radical mechanism. Chain mediators are in particular hydroxyl (HO^\cdot) and hydroperoxyl (HO_2^\cdot) radicals. In aprotic media the hydrogen peroxide decomposition rate decreases due to a change in the mechanism of chain termination. The interaction of the aprotic solvent with hydroxyl radicals results in the formation of secondary radicals that are less reactive in chain propagation steps but are efficient in chain termination processes.

3.2.3. Effect of the pressure

Additional reactions tests were carried out at increased pressure provided by synthetic air in order to evaluate the influence of pressure on the oxidation rate. Table 3 shows that conversion is markedly influenced by the pressure. The reaction at atmospheric pressure proceeds with low conversion (19%). When 10 bar of air were added full conversion was achieved. However when 28 bar of air were added the conversion achieved was only 30%. We suppose that this is the result of two competing phenomena, the oxidation of cyclohexanol and the decomposition of

Table 3
Effect of pressure on cyclohexanol oxidation

Initial synthetic air pressure (bar)	Cyclohexanol conversion (%)	Selectivity (%)		H ₂ O ₂ consumption (%)
		Cyclohexanone	ϵ -caprolactone	
1	19	84	16	30
10	100	100	–	95
28	30	73	27	45

Catalyst = Cs_{2.5}H_{0.5}PW₁₂O₄₀: 120 mg, cyclohexanol: 10 mmol, aqueous H₂O₂ (70 wt%): 40 mmol, solvent: 5 g, *t*: 2 h, *T*: 90 °C.

hydrogen peroxide. When 10 bar were added the additional oxygen mainly contributed to the oxidation of cyclohexanol. When 28 bar were added the enhancement of the hydrogen peroxide decomposition prevailed and the overall conversion was not as high as in the previous case.

3.2.4. Catalyst reuse

Insoluble solid catalysts have practical advantages such as the easiness of separation and reusability. Although the H_{0.5}Cs_{2.5}-PW₁₂O₄₀ catalyst consists of ultrafine particles (micron sized) its separation from the reaction mixture was possible under centrifugation. The isolated catalyst was dried at 110 °C overnight and then reused under the same reaction conditions: 10 mmol of cyclohexanol, 40 mmol of hydrogen peroxide, 5 g of acetonitrile, 120 mg of catalyst and 90 °C reaction temperature. After adjusting the stirring rate and reacting the mixture for 4 h a conversion level was achieved that was about 50% that of the fresh catalyst.

The current study shows that the H_{0.5}Cs_{2.5}PW₁₂O₄₀ catalyst is deactivated during the reaction. No additional tests were however performed in order to find out which were the reason for this activity loss.

4. Conclusions

A H_{0.5}Cs_{2.5}PW₁₂O₄₀ catalyst was prepared in a simple way and characterized by XRD showing similar crystalline properties as its precursor. The acidity of H₃PW₁₂O₄₀ and H_{0.5}Cs_{2.5}PW₁₂O₄₀ were estimated from dehydration of 1-4-butanediol. The HPA and its Cs-salt exhibited very strong acidity, responsible for dehydration at 100 °C.

Besides their similar acidity the Cs-salt showed a higher activity than HPA. The Cs-salt seemingly has a higher surface proton population available for reaction. This is due to a more open structure and a higher specific surface area.

Cyclohexanol oxidation with aqueous hydrogen peroxide as oxidant and H_{0.5}Cs_{2.5}PW₁₂O₄₀ as catalyst depends on both the polarity and the protic/aprotic nature of the solvent. Acetonitrile, the most polar aprotic solvent used, had the best performance.

The partial pressure of oxygen affects both the cyclohexanol oxidation and the hydrogen peroxide decomposition rates. At medium pressures cyclohexanol oxidation is greatly enhanced and full conversion is achieved (compared to 19% conversion at 1 atm). At high pressures the rate of decomposition of hydrogen peroxide is greatly increased and the oxidation of cyclohexanol is no longer complete (30%).

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