

Esterification of propanoic acid by butanol and 2-ethylhexanol catalyzed by heteropolyacids pure or supported on carbon

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Abstract

The esterification of propanoic acid by butanol or 2-ethylhexanol is catalyzed by heteropolyacids pure or supported on carbon supports. A detailed study of the homogeneous reaction has been carried out, showing that the reaction rate is proportional to the concentration of protons and that the catalyst can be easily recycled by distillation of the reaction medium. When the heteropolyacid is supported on carbon, different behaviors are observed, depending on both the heteropolyacid and the carbon support. However, in all cases, the activity is lower than that of the pure heteropolyacid. The activity loss increases with the surface area of the carbon support and, for a given support, it decreases with the polyanion loading. A study of the recycling of these catalysts has shown that a deactivation occurs, due to the redissolution of the polyanion in the reaction medium. This phenomenon is more important for the catalysts having the highest activity per Keggin unit, due to a smaller interaction of the polyanion with the support.

Keywords: Esterification; Heteropolyacids; Carbon supported heteropolyacids

1. Introduction

Heteropolyanions are known to be active catalysts for acid and/or redox reactions, in both homogeneous and heterogeneous systems [1–3]. These compounds are used in some industrial processes such as the hydration of olefins (acid catalysis) [4] and the synthesis of methacrylic acid (redox catalysis) [5,6]. Many polyanionic structures are known but the most popular is the Keggin one which corresponds to the formula $[XM_{12}O_{40}]^{n-}$, M being a transition element (usually molybdenum or tungsten) and X an

heteroelement (such as phosphorus or silicon) [7,8]. It displays a tetrahedral symmetry based on a central XO_4 tetrahedron surrounded by twelve MO_6 octahedra arranged in four groups M_3O_{13} of three edge-bridged octahedra. When the counteraction is the proton, the corresponding heteropolyacids display high acidic properties which can be tuned by changing the M and X elements [2].

Industrially, the most used acid catalysts are the sulfuric and fluorhydric acids. For example, they are used in alkylation, esterification and hydrolysis reactions [9–11]. However, these acid catalysts are toxic and corrosive and, in addition, they are hard to remove from the reaction medium. Due to these considerations and to pollution problems, the challenge is actually to

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replace them by other acid catalysts, and, if possible, solid catalysts easier to remove from the reaction products and to recycle. One example is the sulfonic acids, which are now used both in homogeneous and heterogeneous catalysis. In homogeneous catalysis, *p*-toluene sulfonic acid is a good catalyst, while in heterogeneous catalysis, SO₃H-resins display interesting properties, for example in MTBE synthesis. Heteropolyacids are also good candidates for this purpose and they have been used successfully in acid reactions such as esterification [12,13]. Unfortunately they can only be removed from the reaction medium by distillation, due to their high solubility in polar solvents. As a consequence, many studies were undertaken in order to support these polyacids on oxides or carbons. It appears from literature data that the best supports are carbons [14–17] and the heterogeneous catalysts obtained by this way are now well studied [18,19], even if the interaction between the polyacid and the support is not well understood.

We report here the results on the esterification of propanoic acid by butanol and 2-ethylhexanol both by pure and carbon-supported heteropolyacids. Two heteropolyacids were chosen for these studies, the 12-tungstophosphoric and 12-tungstosilicic acids. Tungstic polyacids were chosen in order to avoid redox reactions, well known to occur with molybdenum compounds. Various carbon supports were studied and their effect on the recycling of the catalysts was also determined.

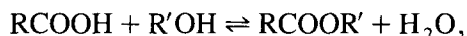
2. Experimental

12-tungstophosphoric and 12-tungstosilicic acids were commercial products from Prolabo. They were recrystallized before use. Their purity was checked by ³¹P and ²⁹Si NMR. Various carbon supports were used: two active charcoals, one from Aldrich (Darco Aldrich, No. 27809-2, *S* = 1500 m² g⁻¹) and one from Strem Chemical (No. 06-0050, *S* = 1000 m² g⁻¹), one

graphite (Lonza HSAG-12, *S* = 310 m² g⁻¹) and two carbon blacks (Vulcan-6 Cabot, *S* = 115 m² g⁻¹ and Vulcan-3 Cabot, *S* = 75 m² g⁻¹).

The HPW/Carbon and HSiW/Carbon catalysts were prepared as in Ref. [14,18] by adsorption from a solution in 0.1 M HCl. After washing with 0.1 M HCl the samples were dried overnight at 373 K. The amount of polyacid in the catalysts was determined by various methods, as in Ref. [18]: polarography, ³¹P and ²⁹Si MAS NMR, potentiometric titration by NaOH and chemical analysis. All methods led to similar results.

The esterification of propanoic acid by butanol or 2-ethylhexanol was carried out in a 250 mL three-necked flask equipped with a Vigreux column and a septum to enable sampling of the liquid phase. The scheme of the apparatus is given on Fig. 1. As the esterification reaction is an equilibrium



complete conversion can only be achieved by elimination of the evolved water. This can be done by forming an azeotrope with an organic solvent such as toluene. After condensation water separated from the organic phase which was then recycled. In order to maintain the temperature quite constant at 333 K and to distil the water/toluene azeotrope, the system was connected to a vacuum line via a pressure regulation system. Typically the pressure in the reaction system was maintained to ca. 2×10^4 Pa. Experimental conditions were as follows: temperature 333 K; toluene 75 mL; propanoic acid 0.3 mol; alcohol 0.3 mol. When catalytic testings were made with other conditions, these will be indicated in the text. In some cases water was not removed. The apparatus was then less complicated, as there was only one reflux condenser on the three neck flask.

In all cases, the kinetics of the reaction was followed by determination of the amount of evolved water and by gas chromatographic analysis of the solution. In all experiments with polyacids, the selectivity of the reaction was

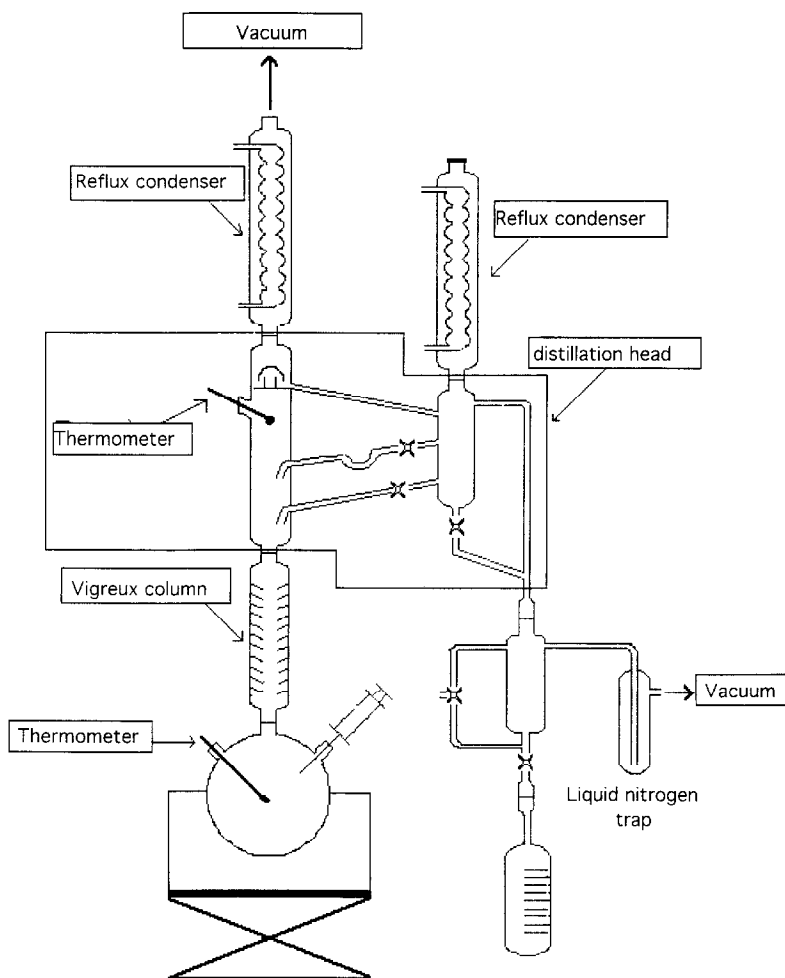


Fig. 1. Scheme of the apparatus used for the esterification of propanoic acid by butanol or 2-ethylhexanol.

> 99% for the ester, no other products being detected by gas chromatography or NMR of the reaction medium (the precision of the analysis methods should allow the observation of very small amounts of other products, typically 1% of the total products for NMR and 0.5% for chromatography).

3. Results and discussion

3.1. Esterification of propanoic acid by the polyacid in solution

3.1.1. Esterification by $H_3PW_{12}O_{40}$

In order to achieve a good reproducibility of the results the heteropolyacid was dried

overnight at 393 K, leading then to the formation of the hexahydrate form. This form of the heteropolyacid was soluble in all reaction media, in contrast to the anhydrous polyacid, and allowed the knowledge of the number of protons in the reaction media with a good precision, as it is relatively stable, in contrast to the other hydrates.

A typical result is given in Fig. 2 for the esterification of propanoic acid by butanol catalyzed by $H_3PW_{12}O_{40}$ (catalyst amount: 1 g corresponding to a ratio substrate/catalyst equal to 900). The equilibrium constant K ,

$$K = \frac{[\text{ester}] \cdot [\text{water}]}{([\text{acid}] \cdot [\text{alcohol}]},$$

can be determined from the conversion at very

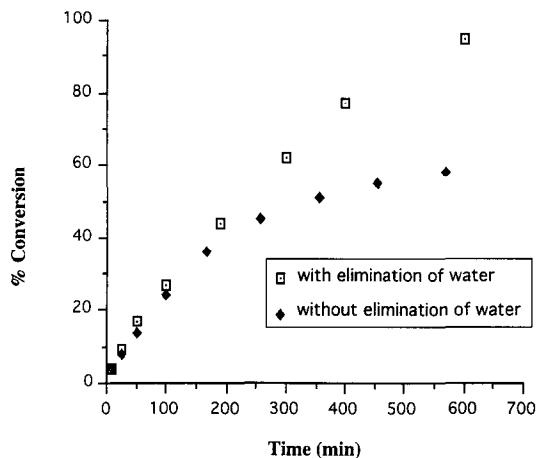


Fig. 2. Esterification of propanoic acid by butanol catalyzed by $H_3PW_{12}O_{40}$ (substrate/catalyst = 900).

long times, when water is not removed by azeotropic distillation. Its value at 333 K is

$$K = 2.7 \text{ (esterification by butanol)}$$

$$K = 1.7 \text{ (esterification by 2-ethylhexanol).}$$

A detailed kinetic study was performed on these systems. First of all, it was checked that the reaction rate was proportional to the amount of heteropolyacid in the reaction medium. Second, a variation of the relative concentrations of acid and alcohol and a modelling of the curves with elimination of the evolved water was achieved. These data allowed to determine that, in a first approximation, the kinetic law could be written as

$$v = k_1 \cdot [\text{HPA}] \cdot [\text{acid}]^{0.3} \cdot [\text{alcohol}]^{0.3},$$

with $k_1 = 1.7 \text{ mol}^{-2} \text{ min}^{-1}$ for butanol and $k_1 = 0.8 \text{ mol}^{-2} \text{ min}^{-1}$ for 2-ethylhexanol. For this purpose, it was assumed that the water concentration in the reaction medium was always negligible, resulting in a simpler kinetic law. However, formally, the kinetic law should be of the form

$$v = k_1 \cdot [\text{HPA}] \cdot [\text{acid}]^a \cdot [\text{alcohol}]^b - k_2 \cdot [\text{HPA}] \cdot [\text{ester}]^c \cdot [\text{water}]^d.$$

Practically, the rate of water elimination from the reaction mixture is determined by the rate of

mass transfer of H_2O steam from the reaction mixture to gas phase. This rate is proportional to water concentration in the solution. To make the water elimination rate equal to the esterification rate needs accumulation of a non-negligible water concentration in the solution. So, in order to determine the true kinetic law, it should be necessary to take into account this fact, leading to a constant water concentration in the reaction medium, while the concentrations of acid, alcohol and ester vary. As our purpose was not to determine the true kinetic law (which should necessitate many other experiments, for example at low concentrations and with various amounts of water in the reaction medium), but only to find an empirical law allowing the modelling of the reaction curves, we did not take into account this concentration. As the experimental results can be modelled by the simple law given above, we can reasonably expect that the water concentration in the reaction medium was very low, even if we did not measure it.

These results show also that the reaction is easier and more complete with butanol than with 2-ethylhexanol, as expected. This law shows a surprising feature as, normally, the reaction rate should be proportional to the concentrations of the acid and of the alcohol. The observed order (0.3) is probably due to various parameters such as the high concentrations of the substrates in the reaction medium and diffusion problems. Indeed the 'kinetic' law was not determined in good conditions, as the concentrations were too high. So, the reaction rate should be, theoretically, proportional not to the concentrations but to the activities, which are very different from concentrations when these latter are high. Diffusion problems occur also probably in so concentrated media.

3.1.2. Comparison between 12-tungstophosphoric acid and 12-tungstosilicic acid

In order to study the influence of the number and of the acid strength of the protons, the two heteropolyacids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$

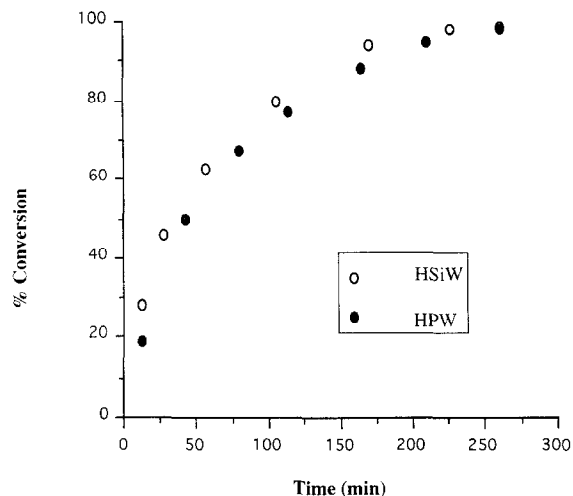


Fig. 3. Comparison of the catalytic activities of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in the esterification of propanoic acid by butanol.

were tested in the esterification of propanoic acid by butanol. This reaction was made with a propanoic acid/butanol molar ratio of 1.33 (0.4 mol of propanoic acid instead of 0.3) and with elimination of the evolved water by formation of an azeotrope with toluene. The amount of polyacid was $5 \cdot 10^{-4}$ mol (corresponding to a ratio alcohol/polyanion of 600). The results are given on Fig. 3 which shows that the activity is always higher with $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. This can be quantified by calculation of the initial reaction rates which are found to be 4.8×10^{-3} mol min^{-1} for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and 6.5×10^{-3} mol min^{-1} for $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. The ratio of these two reaction rates corresponds to the ratio of the number of protons in each polyacid (4/3), showing that the acid strength of the protons of 12-tungstosilicic acid is sufficient to catalyze the esterification reaction and that all protons are active sites.

3.1.3. Recycling of the catalyst

The above study shows that heteropolyacids are good catalysts for the esterification of propanoic acid. However this is not sufficient for a possible industrial application of such systems. Indeed, one of the most important properties for reactions made in batch is to have an easy recycling of the catalyst. For this pur-

pose the reaction was stopped after 5 h and the reaction medium was distilled until dryness. The resulting solid was then reused as catalyst for a new reaction in the same conditions (0.4 mol of propanoic acid, 0.3 mol of butanol, 2.5×10^{-4} mol of HPW and 75 mL of toluene). After four cycles, the conversion at 5 h had only slightly decreased (from 82% to 78%), showing that these polyacids can be easily recycled by this way.

3.2. Esterification of propanoic acid by supported heteropolyacids

3.2.1. Influence of the nature of the support on the catalytic activity

For this purpose the highest polyanion loading was used, in order to have the highest acidic solid from a given support. This highest loading was determined by performing a systematic study of the exchange reaction [20]. It depends greatly on both the polyacid and the support. For example for HPW, it is 50 wt% on the Aldrich active charcoal, 31 wt% on the Strem

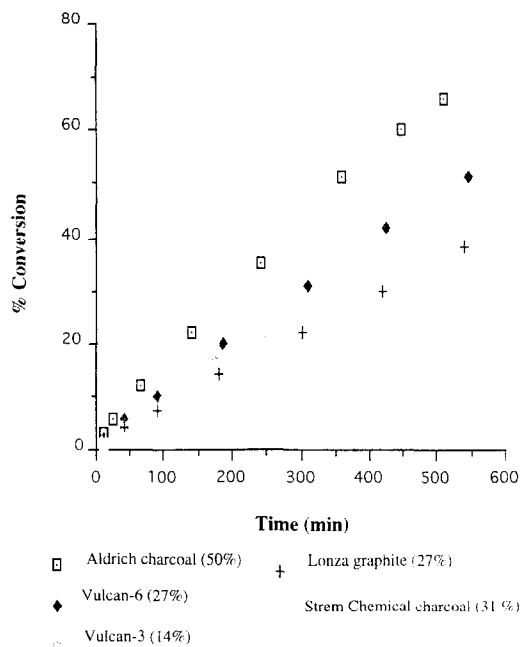


Fig. 4. Comparison of the activities of the various HPW/carbon catalysts in the esterification of propanoic acid by butanol.

Table 1
Apparent proton activity of the HPW/carbon catalysts

Support	Polyanion loading (wt%)	Formulation of the polyacid from butanol esterification	Formulation of the polyacid from 2-ethylhexanol esterification
Aldrich active charcoal	50	$H_{1.1}PW_{12}O_{40}$	$H_{1.0}PW_{12}O_{40}$
Strem chemical active charcoal	31	$H_{0.6}PW_{12}O_{40}$	$H_{0.6}PW_{12}O_{40}$
Lonza graphite	27	$H_1PW_{12}O_{40}$	$H_{0.9}PW_{12}O_{40}$
Vulcan-6	27	$H_{1.4}PW_{12}O_{40}$	$H_{1.4}PW_{12}O_{40}$
Vulcan-3	14	$H_{2.0}PW_{12}O_{40}$	$H_{1.9}PW_{12}O_{40}$

support and 27 wt% on the Lonza graphite and the Vulcan 6 carbon black.

The curves giving the conversion for the $H_3PW_{12}O_{40}$ /carbon catalysts, in the esterification of propanoic acid by butanol, are given on Fig. 4 (ratio substrate/HPW = 100). It can be deduced immediately from these data that the supported polyacid is less active than the unsupported one. The main problem for performing the comparison of homogeneous and heterogeneous catalysts is to know the intrinsic activity of one active site, typically in this case of one proton. We will assume, arbitrary, that this activity is the same for the protons in both the homogeneous and heterogeneous catalysts. We will also assume (and this fact has been verified indirectly by the modelling of the curves giving the conversion as a function of time) that the dependance of the reaction rate to the reagents obeys the same law in the two cases (i.e. we have the same kinetic law). By doing these hypotheses, it is possible to determine what is the real amount of 'active' protons in the solid. This number can be expressed as the mean number of active protons per Keggin unit and can be visualized by the formulas

$H_nPW_{12}O_{40}/C$ or $H_pSiW_{12}O_{40}/C$ with $n < 3$ and $p < 4$. The corresponding values are listed in Tables 1 and 2 for the HPW/C and HSiW/C catalysts, respectively.

The same values are obtained from the esterification by butanol and from the esterification by 2-ethylhexanol. So, the numbers n and p can be seen as a measure of the number of active protons remaining on the solid. An interpretation of this (but not the only one) can be that the interaction polyanion-support is made by an acid-base reaction between some protons of the polyacid and some basic sites of the support, the protons of the polyacid reacting with the basic sites of the support (for example hydroxyl groups) and protonating them. This leads then to an ionic interaction, as previously proposed for silica [21]. The results in Tables 1 and 2 indicate that the highest values of n and p are obtained with the supports having the lowest B.E.T. surface area, in agreement with the above explanation: Indeed, on high surface area supports an encapsulation of the polyanion can occur, leading then to a nearly complete neutralization of the charges, in contrast to what will happen on supports with a low surface area

Table 2
Apparent proton activity of the HSiW/carbon catalysts

Support	Polyanion loading (wt%)	Formulation of the polyacid from butanol esterification	Formulation of the polyacid from 2-ethylhexanol esterification
Aldrich active charcoal	44	$H_{1.3}SiW_{12}O_{40}$	$H_{1.3}SiW_{12}O_{40}$
Vulcan-6	12	$H_{2.6}SiW_{12}O_{40}$	$H_{2.5}SiW_{12}O_{40}$
Vulcan-3	11	$H_{2.9}SiW_{12}O_{40}$	$H_{2.9}SiW_{12}O_{40}$

where the repulsion between the charges will prevent such a phenomenon. However, on these latter the polyanion loading will be smaller and a higher amount of catalyst (polyacid + support) will be necessary in order to have the same results, showing that it will be necessary to find an optimum.

Unfortunately, a microcalorimetric study showed that the interaction between the polyacid and the support is not so simple as described above [18]. Indeed, these results showed that the number of acid sites per Keggin unit was quite the same on the pure and supported phosphotungstic acid, the difference being the acid strength: supporting the polyacid on the carbon support results in a decrease of the acid strength, probably due to a direct interaction between the polyanionic entity with the support via electronic transfers which will have as a consequence a stabilization of the bond with the proton and then a decrease of the acid strength. The numbers n and p should then correspond, in fact, to the mean number of protons having a sufficient acid strength to catalyze the esterification reaction. As the acid strength requirement is at about the same for the esterification by butanol and 2-ethylhexanol, the same values were obtained.

An other explanation to these data should be that there are diffusion problems. Indeed, as we said it above, the numbers n and p decrease when the surface area of the support increases (with the exception of the Strem active charcoal). As the increase of the support area is mainly due to a decrease of the mean pore radius, the diffusion rate of the molecules inside the pores decreases also and then, it is quite possible that only the polyanions near the pore entrances are effectively used for the esterification reaction. The B.E.T. surface area data support also this interpretation. Indeed, it has been found that the mean pore radius is about the same for the Aldrich active charcoal and the graphite (ca. 2 nm) while it is lower for the Strem Chemicals active charcoal. No pores are found on the carbon blacks. However, even if

this phenomenon should be taken into account for the supports with a high surface area, it cannot explain why only one proton per Keggin unit remains inactive for the polyacids supported on the carbon blacks and it is also reasonable to think that this proton is used for the interaction with the support.

3.2.2. Influence of the polyanion loading on the catalytic activity for HPW supported on the Aldrich active charcoal

Different catalysts were prepared by introducing various amounts of phosphotungstic acid on the Aldrich active charcoal. The polyanion loading was varied between 10 and 50 wt%. These catalysts were studied in the esterification of propanoic acid by butanol and the corresponding $H_nPW_{12}O_{40}/C$ formulations were determined. The value of n was found to be 0.5, 0.7, 0.9 and 1.1 for polyanion loadings corresponding to 10, 20, 30 and 50 wt% respectively. These results are in agreement with those previously reported by Schwegler and van Bekkum for the esterification of phthalic anhydride by 2-ethylbutanol [12]. They are also in agreement with the above explanation, the first polyanions going in positions where their interaction with the support will be the higher or, in other words, where the highest electronic transfers will occur.

The consequence of this is that the best catalyst will always be the solid having, for a given support, the highest polyanion loading.

3.2.3. Recycling of the catalyst

Various parameters were studied, such as the treatment of the catalyst before the recycling, the nature of the alcohol and the nature of the catalyst (polyanion and support).

First of all, different treatments of the catalyst were made before recycling and their effect on the catalytic activity was studied. For this purpose, the catalyst was separated by filtration from the reaction medium and reused immediately without any washing or dried overnight at 413 K. The results for HPW supported on the

Vulcan-6 carbon black (HPW loading 27 wt%, ratio substrate/HPW = 100) in the esterification of propanoic acid by butanol are given on Fig. 5. It can be seen immediately that the dried catalyst was less active than that which was reused immediately after filtration. In the case of this latter solid, the deactivation was due to a small redissolution of the polyanion in the reaction medium, as proved by chemical analysis. For example, after one cycle the polyanion loading has decreased from 27 wt% to 23 wt%. The loss of activity when the catalyst was dried can be explained, in addition to the redissolution of the polyanion, by a poisoning of the active sites by carbonaceous residues formed during the heating at 413 K.

The same results were obtained for the phosphotungstic acid supported on the Aldrich active charcoal. As above, there was a decrease of activity for the dried catalyst compared to that was reused immediately. In this case a reduction of the B.E.T. surface area (from $450 \text{ m}^2 \text{ g}^{-1}$ to $270 \text{ m}^2 \text{ g}^{-1}$) and of the microporous volume (from $52 \text{ cm}^3 \text{ g}^{-1}$ to $33 \text{ cm}^3 \text{ g}^{-1}$) was also observed, in agreement with a poisoning effect. In addition, as expected, the activity decrease is

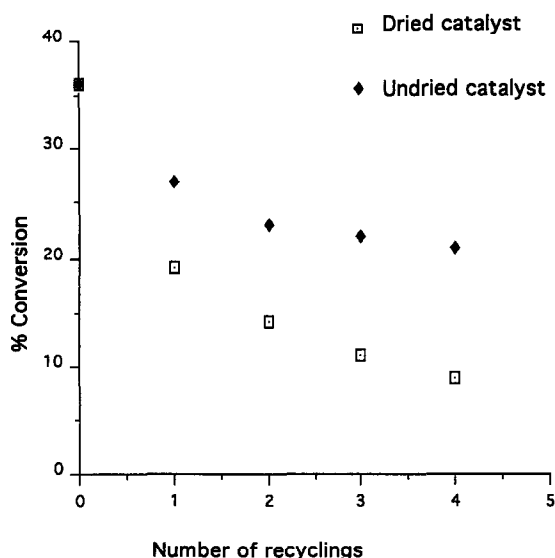


Fig. 5. Conversion after 5 h of reaction, in the esterification of propanoic acid by butanol, for HPW/Vulcan-6 catalysts dried or not as a function of the number of recyclings.

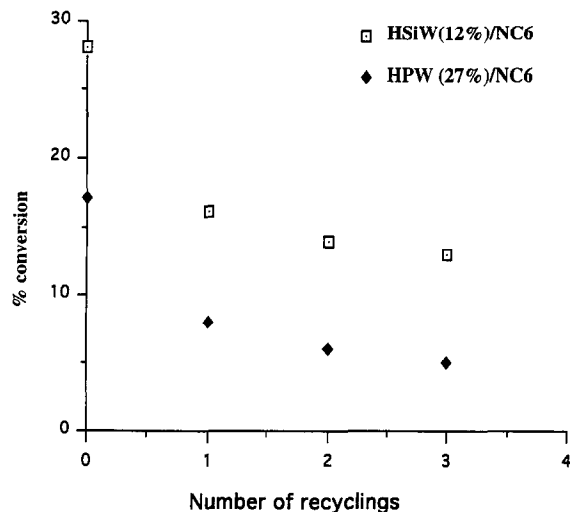


Fig. 6. Conversion after 5 h of reaction, in the esterification of propanoic acid by butanol for the HPW/Vulcan-6 and HSiW/Vulcan-6 catalysts.

smaller than for HPW supported on Vulcan-6 (less than 5% after 5 recyclings) showing that, from the point of view of the recycling, the best catalyst is that which has the lowest value n in its formulation.

When the alcohol is the 2-ethylhexanol, the same behavior is observed but the loss of polyanion is higher (for example, in the case of the Vulcan-6 carbon black the polyanion loading decreases from 27 wt% to 14 wt%, instead of 23% for butanol). This can be explained by an adsorption competition, on the support, between the alcohol and the polyanion: The alcohol can be sorbed on the carbon, as the polyanion, as so, there is an equilibrium between the species in solution (polyanion + alcohol) and the sorbed species. In the case of butanol, the polyanion is much more strongly sorbed than the alcohol and it desorbs only slightly. In contrast, 2-ethylhexanol will be more strongly adsorbed and so it will lead to a more important desorption of the polyanion. This can be seen easily by stirring the catalyst in a solution containing 2-ethylhexanol. A ^{31}P NMR study of the solution after stirring during some hours shows that it contains the polyanion. Similarly, the

catalytic activity of the resulting solid has decreased drastically.

Finally, the effect of the nature of the heteropolyacid has been studied. In order to better visualize this effect, the system chosen for this study was that which showed the higher deactivation: the esterification by 2-ethylhexanol and the polyanion supported on the Vulcan-6 carbon black. The results are given on Fig. 6 (for a substrate/polyanion ratio of 100). Quite the same curve was obtained for the two systems but the silicotungstic acid led always to more active catalysts, showing that it should be a better candidate for an industrial use.

4. Conclusion

12-phosphotungstic and 12-silicotungstic acids are active catalysts for the esterification of propanoic acid by butanol or 2-ethylhexanol. The reaction is totally selective for the formation of the ester and water and can be performed until a conversion of 100% is reached by elimination of water by azeotropic distillation. The catalytic activity is proportional to the number of protons, and so the 12-silicotungstic acid is the most active system, per Keggin unit. These catalysts can be easily recycled by distillation, and only a small loss of activity is observed.

Carbon-supported heteropolyacids are also active catalysts for the esterification of propanoic acid. However their activity per Keggin unit is always lower than that of the pure heteropolyacid. It depends also on many parameters such as the support, the heteropolyacid and the polyanion loading. The best results are achieved with supports having a low surface area (but in this case the highest possible

polyanion loading is small), the silicotungstic acid and a polyanion loading as high as possible. These catalysts can be recycled after a simple filtration. The activity loss is due to a redissolution of the polyanion and increases when the surface area of the support decreases. It is also higher for the esterification of 2-ethylhexanol than for that of butanol.

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