

Hydration and acetoxylation of dihydromyrcene catalyzed by heteropoly acid

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Received 24 April 1996; revised 23 September 1996; accepted 27 September 1996

Abstract

The liquid-phase hydration and acetoxylation of the monoterpene dihydromyrcene (DHM, 3,7-dimethyl-1,6-octadiene) are efficiently catalyzed by Keggin-type heteropoly acid $H_3PW_{12}O_{40}$ (HPA) at 14–30°C to yield dihydromyrcenol (DHM–OH, 2,6-dimethyl-7-octen-2-ol) and dihydromyrcenyl acetate (DHM–OAc). Homogeneous, biphasic (DHM/AcOH–H₂O–HPA) and heterogeneous (with HPA/SiO₂ catalyst) reactions have been studied. HPA has a much higher catalytic activity than conventional acid catalysts such as H₂SO₄ and Amberlyst-15. A synthetically useful biphasic acetoxylation/hydration of DHM has been developed. The method provides a 90% selectivity to the sum of DHM–OH and DHM–OAc at 21% DHM conversion and allows for easy and clean catalyst recycling without loss of activity.

Keywords: Acetoxylation; Dihydromyrcene; Heteropoly acid; Hydration

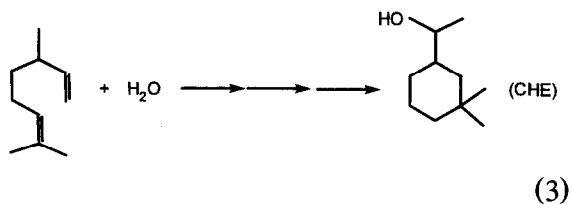
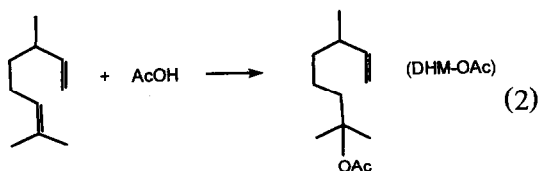
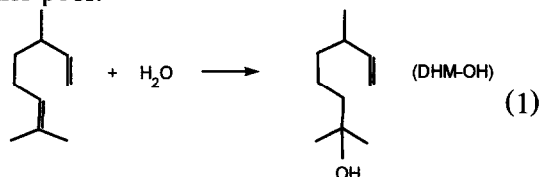
1. Introduction

Acid-catalyzed hydration and acetoxylation of terpenes are important as synthetic routes to terpene alcohols and esters which are useful in perfumery and flavoring compositions [1]. Thus, such perfume ingredients as dihydromyrcenol (DHM–OH, 2,6-dimethyl-7-octen-2-ol) and dihydromyrcenyl acetate (DHM–OAc) are prepared on an industrial scale by the hydration (Eq. (1)) and acetoxylation (Eq. (2)) of dihydromyrcene (DHM, 3,7-dimethyl-1,6-octadiene).

The process is complicated by acid-catalyzed DHM isomerization and cyclization [2–6]. The latter side reaction leads to 1-(3,3-dimethylcyclohexyl)ethanol (CHE) (Eq. (3)) [5]. Direct hydration of DHM is a difficult process; it proceeds only with concentrated mineral acids. Thus, contacting DHM with 60–80% aqueous H₂SO₄ at 0–5°C affords DHM–OH with 70% selectivity at 85% DHM conversion [2]. However, the disposal of H₂SO₄ has become a serious environmental problem. An easier way to obtain DHM–OH is the acetoxylation of DHM with AcOH to DHM–OAc — which is itself useful — followed by hydrolysis of DHM–OAc to DHM–OH [3–5] or the conversion of DHM into a mixture of the terpene alcohol and the (chloro)acetate by interacting DHM with aqueous acetic acid or chloroacetic

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acid [6]. In acetoxylation, Eq. (2), solid acid catalysts such as cation exchange resins [3,4,7,8] and synthetic zeolites [9,10] have been employed. However, their catalytic activities are rather poor.



Heteropoly acids (HPAs), especially those of the Keggin series, e.g. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo), etc., are promising acid catalysts for the synthesis of fine and specialty chemicals [11–14]. HPAs are industrially employed as catalysts for the liquid-phase hydration of olefins [14]. They have also been used for the acetoxylation of olefins [15,16]. HPAs are highly soluble in water and polar organic solvents, such as lower alcohols, ethers, ketones, carboxylic acids, etc., scarcely soluble in less polar organic substances and insoluble in hydrocarbons [11]. This provides an opportunity of carrying out acid-catalyzed liquid-phase reactions in two-phase systems with easy separation of products from HPA catalyst which otherwise, with conventional liquid acid catalysts, proceed homogeneously. Several examples of such biphasic reactions have been reported, e.g. polymerization of tetrahydrofuran [14,17], esterification of 4-nitrobenzoic acid [12], alkylation of

hydroquinone [18], and trimerization of aldehydes [19].

In this paper, we report on the application of the Keggin-type HPAs, in particular PW, the strongest HPA known so far [11,12], as catalysts for the liquid-phase hydration and acetoxylation of DHM (Eqs. (1) and (2)). Homogeneous, biphasic and heterogeneous systems have been studied. A practical method to convert DHM into a DHM-OH + DHM-OAc mixture in a two-phase liquid/liquid system has been developed.

2. Experimental

2.1. Materials

$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 28\text{H}_2\text{O}$ (Janssen Chimica), Amberlyst-15 (Aldrich) and acetic acid $\geq 99\%$ (Baker) were of commercially available purity. DHM 90% and reference samples of DHM-OH, DHM-OAc, 1-(3,3-dimethylcyclohexyl)ethanol and 1-(3,3-dimethylcyclohexyl)ethyl acetate were obtained from Quest International (Ashford, UK). 10–50% HPA/ SiO_2 catalysts were prepared by impregnating Aerosil 380 (Degussa) with an aqueous HPA solution, followed by drying at $130^\circ\text{C}/0.2\text{--}0.3$ mmHg for 1.5 h.

2.2. NMR spectroscopy

^{31}P NMR MAS and solution spectra were measured on a Varian VXR-400S spectrometer as described elsewhere [20]. 1% H_3PO_4 in D_2O was used as an external reference.

2.3. Reactions

The hydration and acetoxylation of DHM were carried out batchwise in a 75 ml double-walled glass reaction vessel equipped with a magnetic stirrer. Major products, DHM-OH and DHM-OAc, as well as byproducts, 1-(3,3-di-

methylcyclohexyl)ethanol (CHE) and 1-(3,3-dimethylcyclohexyl)ethyl acetate (CHEA) [5], were identified by GLC using authentic samples. GC analyses were performed on a HP 5890 instrument: FID, 25 m × 0.32 mm column with CP Sil 5 CB stationary phase. Undecane was used as a reference to determine response factors (wt.): DHM (0.99), DHM–OH (1.24), DHM–OAc (1.37), CHE (1.24) and CHEA (1.40). Unconverted DHM was measured, assuming the same response factor for DHM and all its isomerization products.

2.3.1. Homogeneous acetoxylation

The homogeneous acetoxylation was performed by adding DHM (0.1–1.3 M) to a 0.002–0.005 M (0.5–1.5 wt%) $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ solution in AcOH pre-thermostatted at 20–40°C. At appropriate time intervals, aliquots were taken, diluted with hexane (to precipitate HPA) and analyzed by GLC.

2.3.2. Biphasic reactions

The direct hydration of DHM was performed in a two-phase system by contacting 2.0 g of DHM (14 mmol, upper phase) with 8.0 g of 33–71 wt% PW aqueous solution (bottom phase) at 50–70°C for 1–4 h with vigorous stirring. Under such conditions, the amount of DHM and its hydration products in the aqueous phase as well as the amount of HPA in the organic phase were negligible. Eventually, the organic phase was separated in a separatory funnel and products were determined by GLC. The aqueous catalyst phase was recycled without loss of activity.

The combined acetoxylation/hydration in a two-phase system DHM/AcOH–H₂O–HPA was carried out by contacting 1.5–4.0 g (11–28 mmol) of DHM (upper phase) with 8.0 g of 50–70 wt% HPA solution in AcOH–H₂O (50/50–77/23 v/v) at 20–30°C for 1–5 h with vigorous stirring, unless otherwise stated. The upper (product) phase was separated and the products were determined by GLC. The catalyst phase can be re-used by adding fresh

DHM, but for sustainable performance and to prevent HPA precipitation, the loss of AcOH and H₂O due to the reaction and product isolation must be compensated for by adding a calculated amount of AcOH and of H₂O after each run. Eventually, the catalyst phase was diluted with water and extracted with hexane to isolate the remaining products and DHM. The addition of water caused a substantial hydrolysis of DHM–OAc.

2.3.3. Heterogeneous acetoxylation with HPA/SiO₂ catalyst

This reaction was performed by contacting 5.0 g of a stoichiometric 1/1 molar mixture of DHM–AcOH with 0.1–0.5 g of 10–50 wt% HPA/SiO₂ at 14–20°C for 0.5–2 h with intense stirring. Care must be taken as to leaching of HPA from the catalyst. A simple test was used to qualitatively indicate any leaching: Diluting the filtered mixture with hexane (ca. 5-fold). A white HPA precipitate appeared if significant leaching had occurred. To prevent HPA leaching, one must refrain from contacting the catalyst with neat AcOH. No leaching at molar ratios of DHM/AcOH > 1/3 (50/50 v/v) was observed, but at higher AcOH concentration, some PW leaching took place. After reaction, when the stirring had stopped, the catalyst quickly settled. It was filtered off, the filtrate was diluted with hexane and analyzed by GLC. The catalyst was washed with hexane and re-used.

3. Results and discussion

3.1. Homogeneous acetoxylation

With PW as Brønsted acid catalyst, acetic acid adds easily, at 20–40°C, to the most reactive double bond of DHM to form DHM–OAc (Eq. (2)). The reaction reaches an equilibrium at ca. 30% DHM conversion (Fig. 1). The process is strongly complicated by acid-catalyzed isomerization of DHM, yielding a number of

unidentified DHM isomers, as well as by DHM cyclization. Liquid-phase double bond and *cis-trans* isomerization of olefins catalyzed by HPA has been reported elsewhere [21]. The cyclization of DHM, seemingly irreversible, gives rise to the slow formation of CHEA as a secondary acetoxylation product [5]. As a result, the selectivity to DHM-OAc quickly decreases with increasing DHM conversion (Fig. 1), as it does with increasing temperature. In addition to DHM-OAc, 6–10 mol% DHM-OH is also formed, as the reaction mixtures always contain traces of water, which is a more efficient nucleophile than AcOH [22]. The molar catalytic activity of PW in DHM acetoxylation is 80 times higher than that of H₂SO₄, as found from initial reaction rates. This is in accordance with the acid strengths of PW and H₂SO₄ in AcOH (*pK*₁ 4.8 and 7.0, respectively [11]). It is worth noting that HPA can be easily recovered by simply precipitating HPA from the reaction mixture with a hydrocarbon solvent, e.g. hexane.

HPA-catalyzed homogeneous acetoxylation

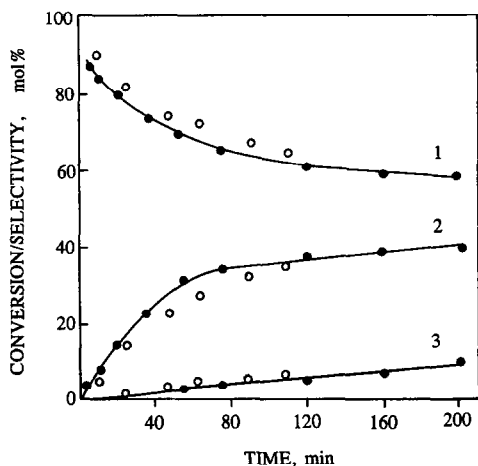
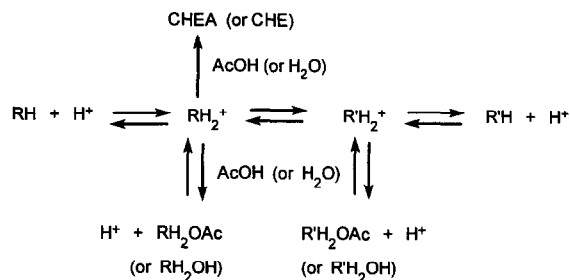


Fig. 1. Homogeneous (closed circles) and heterogeneous (open circles) acetoxylation of DHM catalyzed by PW at 20°C in AcOH: (1) selectivity to DHM-OAc + DHM-OH, (2) DHM conversion and (3) selectivity to CHEA. Homogeneous reaction: 0.005 M (1.5 wt%) PW and DHM/AcOH 1:10 mol/mol; DHM-OAc/DHM-OH product molar ratio: 90/10. Heterogeneous reaction: 2.0 wt% of 40 wt% PW/SiO₂ and DHM/AcOH 1:1 mol/mol; DHM-OAc/DHM-OH molar ratio: 94/6.



Scheme 1.

of 1-hexene to 2-hexyl acetate has been reported [16]. The reaction reached an equilibrium at around 90% 1-hexene conversion at 110°C. Keggin-type HPAs — PW the most efficient — were found to be 30–90 times as active as H₂SO₄, slightly ranging in their activity within a factor of 3 in agreement with their acid strength in AcOH.

The acetoxylation of DHM can well be represented within the framework of carbenium ion mechanism [22] as shown in Scheme 1, where RH and R'H are DHM and a DHM isomer, respectively.

The protonation of DHM generates the carbenium ion, RH₂⁺. This can be subjected to nucleophilic attack by AcOH (or H₂O) to give DHM-OAc (or DHM-OH). Alternatively, RH₂⁺ can isomerize to R'H₂⁺ to further give a DHM isomer, R'H, or its acetate and alcohol. In addition, in a slow and apparently irreversible process, RH₂⁺ can cyclize and form a cyclic alcohol or its acetate (e.g. CHE and CHEA). Thus one can expect that the more efficient the nucleophile is the slower the isomerization and cyclization take place.

3.2. Biphasic reactions

3.2.1. Direct hydration of DHM

The direct hydration of DHM to DHM-OH (Eq. (1)) in the two-phase system, DHM/H₂O-PW, proceeds slowly due to a very low solubility of DHM in water. Elevated temperatures (60–80°C) and high HPA concentrations (60–70

Table 1
Two-phase hydration of DHM to DHM–OH catalyzed by PW aqueous solution

H ₃ PW ₁₂ O ₄₀ (wt%)	T (°C)	τ (min)(%)	Conversion (mol%)	Selectivity
33	50	80	1.0	95
63	50	80	3.1	91
63	60	120	5.6	90
63	70	120	6.7	76
63	80	180	15	39
71	60	60	5.5	91
71	60	120	6.4	79
71	60	180	7.6	71
71	60	260	10	63

wt%) are needed, which makes the reaction non-selective. The selectivity to DHM–OH goes quickly down as the DHM conversion exceeds 5% (Table 1); a large number of byproducts is formed. At DHM conversions of 6–15%, a significant amount of CHE is formed. Although the catalyst is easily recyclable, the reaction is synthetically unsound because of low selectivity.

3.2.2. Acetoxylation/hydration of DHM in two-phase system

Addition of acetic acid to the DHM/H₂O–PW system increases the solubility of DHM in the catalyst phase and thereby greatly enhances the reaction rate. The reaction, which is now a combined acetoxylation/hydration, proceeds readily at 20°C with a much higher selectivity to DHM–OH + DHM–OAc (Table 2) compared to the homogeneous acetoxylation and direct

hydration of DHM. Thus, a 90% selectivity to DHM–OH + DHM–OAc can be obtained at 21% DHM conversion, which is synthetically useful. The selectivity to CHE + CHEA is less than 1%. About 10% of DHM is converted to DHM isomers. No significant polymerization of DHM was observed at 10–20% DHM conversion. Mechanistically, the increase in selectivity can be explained as a result of efficient trapping of the RH₂⁺ carbenium ion by water molecules — which are more nucleophilic than AcOH — thus preventing the isomerization and cyclization of DHM (Scheme 1). The molar ratio DHM–OH/DHM–OAc is 80/20–70/30 in the product phase; after work-up, it is 96/4–85/15 due to DHM–OAc hydrolysis. In the absence of HPA, a 50/50 v/v DHM–AcOH mixture turns to a two-phase system when adding ca. 5% water based on AcOH. With HPA, the phase separation takes place even at lower [H₂O], depending on the HPA content. In such a system, DHM and AcOH as well as reaction products are distributed between the two phases. Yet DHM and reaction products accumulate (80–90%) in the upper phase whereas AcOH is mainly in the bottom (catalyst) phase. Importantly, HPA was practically entirely in the catalyst phase, thus enabling easy and clean catalyst recycling.

Fig. 2 shows the catalyst recycling behaviour in the biphasic acetoxylation/hydration of DHM. It is seen that the activity (conversion) and selectivity are practically constant, 89–92%

Table 2
Acetoxylation/hydration of DHM catalyzed by PW in two-phase system DHM/AcOH–H₂O–PW

PW (wt%)	AcOH–H ₂ O (vol%)	DHM (mmol)	T (°C)	τ (min)	Conversion (%)	Selectivity ^a (mol%)
70	50/50	11	50	210	30	58
70	63/37	11	50	210	47	54
62	74/26	11	20	300	15	95
68	77/23	11	20	180	21	90
68	77/23	11	20	210	29	88
68	77/23	28	30	120	16	93
68	77/23	22	30	300	35	84
54 ^b	77/23	22	30	90	60	57

^a Selectivity to DHM–OH + DHM–OAc based on DHM charged; after work-up, the molar ratio DHM–OH/DHM–OAc: 96/4–85/15. The selectivity to CHE + CHEA was within 0.5–0.8%.

^b H₃PMo₁₂O₄₀; selectivity to CHE + CHEA: 6%.

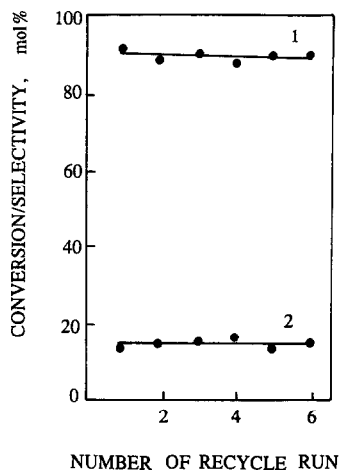


Fig. 2. Recycling of catalyst in the biphasic acetoxylation/hydration of DHM (28 mmol) with 68 wt% PW in AcOH–H₂O 73/23 v/v (8.0 g), 30°C, 2 h: (1) Selectivity to DHM–OH + DHM–OAc and (2) DHM conversion.

and 14–16%, respectively, during 6 runs. Initially colorless, the catalyst phase turned brown during the reaction, but no loss of activity was observed. Nor did HPA decomposition take place, as is clearly seen from ³¹P NMR spectra of the catalyst phase before and after use (Fig. 3). The spectra contain only the well-known line at –15.7 ppm from PW.

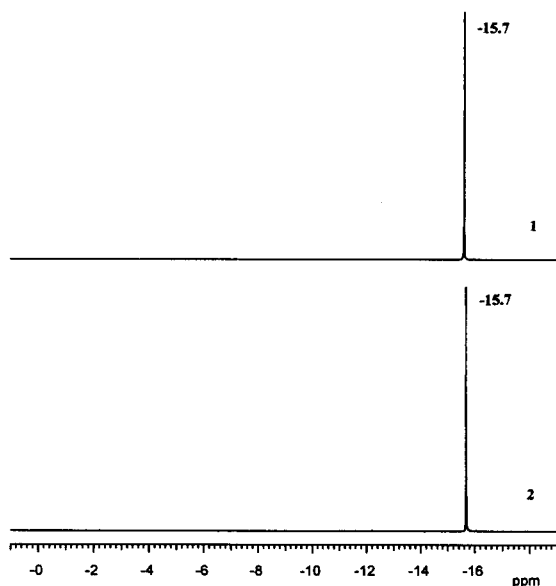


Fig. 3. ³¹P NMR spectra of the 68 wt% PW catalyst solution in AcOH–H₂O 77/23 v/v before (1) and after (2) use.

Table 3

Acetoxylation of DHM with solid acid catalysts (DHM/AcOH 1:1 mol/mol)

Catalyst ^a (wt%)	<i>T</i> (°C)	<i>τ</i> (min)	Conversion (%)	Selectivity ^b (mol%)
PW (5.0)	20	60	< 1	—
Amberlyst-15 (10.0)	20	240	3.1	68
25% PW/SiO ₂ (2.0)	20	30	2.6	91
25% PMo/SiO ₂ (2.0)	20	30	12	57
40% PW/SiO ₂ (2.0)	20	25	13	84
40% PW/SiO ₂ (2.0)	14	30	7.9	90
50% PW/SiO ₂ (2.0)	14	45	10	88

^a In parentheses, catalyst amount in total reaction mixture.

^b Selectivity to DHM–OAc + DHM–OH based on DHM charged; DHM–OH/DHM–OAc molar ratio: 4/96–7/93. At DHM conversion of 8–13%, the selectivity to CHE + CHEA was within 0.6–1.0%.

PMo showed a rather high activity but low selectivity in converting DHM (Table 2). PMo was quickly reduced by the reaction mixture, which made it difficult to separate the catalyst from the product phase. Similarly, PMo reduction was observed in 1-hexene acetoxylation [16].

3.3. Heterogeneous acetoxylation with PW/SiO₂ catalyst

Silica, due to its inertness towards HPA, is the most widely used support for solid HPA catalysts. The state and acidity of PW on SiO₂ have been reviewed elsewhere [12]. The acetoxylation of DHM with 35–50% PW/SiO₂ catalysts proceeds similarly to the homogeneous acetoxylation (Fig. 1, Table 3). The catalytic activities of PW in the two cases are comparable, while the selectivity of the solid catalyst (88–90% at 8–10% conversion) is higher than that of the homogeneous counterpart, less than 1% CHE + CHEA being observed. Probably this is because it is more difficult for the RH₂⁺ cation to isomerize on the catalyst surface than in solution. The PW/SiO₂ catalyst, initially a white powder, turned brown after use. It was readily recoverable by filtration and could be used repeatedly (four times) without loss of

activity. But further, a gradual deactivation was observed probably due to blocking of acid sites by DHM oligomers. With a stoichiometric 1:1 DHM–AcOH mixture, no PW leaching from the catalyst was observed (see Section 2). No decomposition of PW after reaction was found either, as seen from ^{31}P MAS NMR spectra of the 40% PW/SiO₂ catalyst before and after use (Fig. 4). Both spectra contain only one line from neat PW.

Thermal pre-treatment of PW/SiO₂ removes water from the catalyst and strongly enhances its activity. Optimally, this is done by pre-heating the catalysts at 130°C/0.2–0.3 mmHg for 1.5 h. The activity of PW/SiO₂ based on the total amount of PW in the catalyst depends dramatically on the PW loading, reaching a maximum at 35–40 wt% PW loading (Fig. 5). Similar dependencies have been reported and explained as the result of a decrease of the HPA acid strength at lower loadings due to interaction of HPA with surface silanol groups [23].

PW/SiO₂ showed much higher activity than Amberlyst-15, which is not unexpected [11]. Surprisingly, bulk PW showed a very low activity, if any. This can be explained by the small

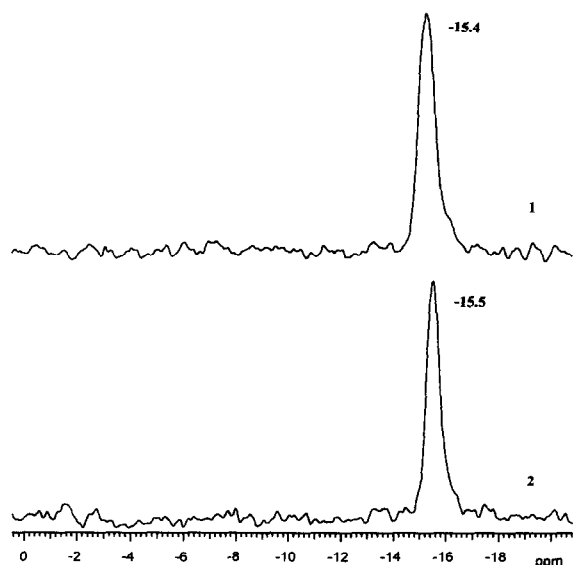


Fig. 4. ^{31}P MAS NMR spectra of the 40 wt% PW/SiO₂ catalyst before (1) and after (2) use.

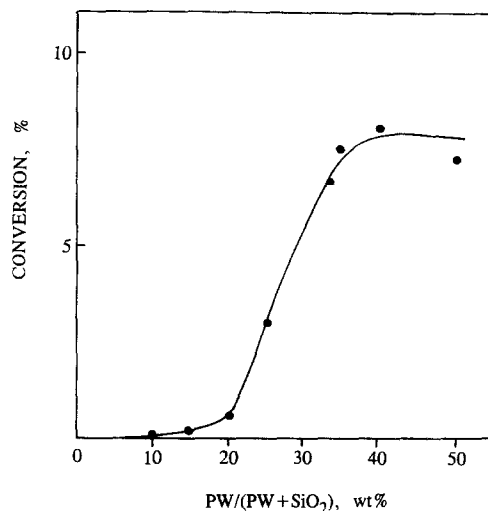


Fig. 5. Conversion versus HPA loading for the acetoxylation of DHM catalyzed by PW/SiO₂ at constant amount of PW (0.80 wt%) in DHM/AcOH 1:1 mol/mol mixture, 14°C, 30 min.

surface area of bulk PW ($1\text{--}5\text{ m}^2\text{ g}^{-1}$). Therefore the amount of accessible proton sites in bulk PW is about 10^2 times less than in the SiO₂-supported PW. Also the deactivation of very strong proton sites of the bulk PW may take place due to adsorption of DHM or reaction products, while the weaker proton sites in the supported catalyst are less susceptible to such site blocking.

As in biphasic system, PMo/SiO₂ exhibited a high activity but low selectivity in the DHM acetoxylation (Table 3). Again, PMo was reduced during the reaction; a fine suspension of the reduced PMo dispersed over both phases, making it difficult to recover the catalyst.

4. Conclusion

The Keggin-type HPA, H₃PW₁₂O₄₀, is the active catalyst for the hydration and acetoxylation of DHM to DHM–OH and DHM–OAc. The HPA shows much higher catalytic activity than conventional acid catalysts such as H₂SO₄ and Amberlyst-15. The uncommon solubility properties of HPA have been profitably ex-

ploited to develop a practical method of the combined acetoxylation/hydration of DHM in two-phase system, providing a 90% selectivity to the sum of DHM–OH and DHM–OAc at 21% DHM conversion as well as easy and clean catalyst recycling without loss of activity.

Acknowledgements

The authors are thankful to Dr. J.A. Peters and Mr. K.R. Kloetstra from TU Delft for the help in NMR measurements (J.A.P.) and preliminary experiments (K.R.K.). Stimulating discussions with Mr. C. Newman, P.N. Davey and C. Richardson (Quest Int.) are highly appreciated.

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