Esterification of mandelic acid catalyzed by heteropoly acid

Ezzat Rafiee [a,b,*], Mohammad Joshaghani [a,b], Fariba Tork [a],
Akram Fakhri [a], Sara Eavani [a]

[a] Department of Chemistry, Faculty of Science, Razi University, Kermanshah 67149, Iran
[b] Kermanshah Oil Refining Company, Kermanshah, Iran

Abstract

The efficacy of various supported heteropoly acids in synthesis of mandelates from mandelic acid and alcohols is investigated. Dodecatungestophosphoric acid (PW) supported on silica gives the best yield in short reaction times. The present procedure represents a clean, practical, simple, mild, time-saving, and eco-friendly method for synthesis of mandelates in short reaction times and excellent yields with 100% selectivity. The catalyst is found to be stable, highly efficient, reusable, and inexpensive during all runs.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Supported heteropoly acid; Mandelate; Heterogeneous catalyst; Esterification reaction

1. Introduction

Heteropoly acids (HPAs) with Keggin structure possess special characteristics that allow their use as catalysts in acid reactions, as they have a very high intrinsic acidity [1]. However, due to the low surface area of the bulk HPA, it is advisable to support them on a carrier with high surface area such as silica, activated carbon, alumina, or clays [2–7]. Another alternative approach is to prepare HPA-salts by partially exchanging protons of the parent HPAs with large cations, such as Cs^+ which present a surface area $100 \, m^2/g$ [8]. The use of a support that leads to good dispersion of the HPA on a high surface area can result in an increase of the catalytic activity [9]. In the design of this type of supported catalyst, the porous structure is an aspect to be taken into account. The pore size must be adequate in order that the molecule transport to or from the active sites can be made easier. Besides, good HPA immobilization in the support is a subject to be carefully considered for the use of the catalysts in liquid-phase reactions.

In our previous studies [10,11], it was proved that silica is a support with suitable properties to obtain HPA-based catalysts for acid reactions. The aim of the present work is to study the use of an efficient catalyst based on heteropoly acid supported on silica, particularly dodecatungestophosphoric acid (PW), and its comparison with molybdophosphoric acid (PMo), supported on different solids in preparation of mandelates. Also, efficacy of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) as a heterogeneous catalyst has been checked.

Mandelates are used in artificial flavourings and perfumes. They are also employed as precursors for synthesis of a number of medicines and pesticides. The repellent effect against mosquitoes of certain esters (methyl, ethyl, butyl, and hexyl) of mandelic acid has been reported by Morton and co-workers [12–14]. Piper [15] in reporting results of entomological tests in Canada, rated ethyl mandelate as one of the best repellents against mosquitoes and black flies. There are a few methods in literature available on the preparation of mandelates [16–22]. However, some of these procedures are not entirely satisfactory and suffer from one or more of the following drawbacks: corrosivity of the strong acids, tedious work-up, low yields, long reaction times and side reactions such as carbonization, oxidation, etherification, etc. As a result, there is still a need for new, mild, convenient and universally applicable methods for synthesis of mandelates.

* Corresponding author at: Department of Chemistry, Faculty of Science, Razi University, Tagh-Bostan, Kermanshah 67149, Iran. Tel.: +98 831 427 4559; fax: +98 831 427 4559.

E-mail address: e.rafiei@razi.ac.ir (E. Rafiee).

2. Experimental

2.1. Techniques

Surface area and porosity of HPA catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Thermogravimetric analyses (TGA) were performed using PerkinElmer TGA 7 instrument under nitrogen flow. IR spectra were recorded with KBr pellets using a Shimadzu 470 spectrophotometer and FTIR spectra were performed using Bomem MB 104 spectrophotometer. Tungsten content in the catalysts was measured by inductively coupled plasma (ICP atomic emission spectroscopy) on a Spectro Ciros CCd spectrometer. Melting points were determined using a digital Gallenkamp apparatus.

2.2. Materials and catalysts

All chemical reagents and solvents were analytical grade and used without further purification. $H_3PW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ hydrate from Aldrich, Merck and Aerosil 300 silica from Degussa were used. Carbon, K10 and KSF montmorillonite clay were obtained from Fluka. γ-Alumina was obtained from Aldrich.
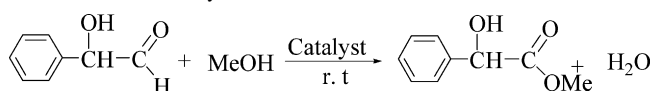
2.3. Preparation of the catalysts

Silica-supported HPA catalysts were prepared by impregnating Aerosil 300 silica (S_{BET}, 300 m^2/g) with an aqueous solution of HPA (with concentrations depending upon the loading required to the support 20, 40, and 60 wt.% PW). The mixture was stirred overnight at room temperature, followed by drying using a rotary evaporator, as described elsewhere [23]. The acidic salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), PW/K10, PW/KSF, PW/γ-Al_2O_3, and PW/C were prepared by the literature methods and fully characterized as reported elsewhere [2–7,23].

2.4. General procedure for the esterification of mandelic acid

A mixture of mandelic acid (3 mmol), alcohol (15 mL) and appropriate amount of the catalyst (according to Table 1) was stirred at room temperature for the length of time as indicated in Table 2. Progress of the reaction was monitored by TLC. After completion of the reaction, evaporating the excess of alcohol and diluting the residue with ether (30 mL), the catalyst was filtered off and washed with ether (2× 15 mL). The filtrate was treated with 5% sodium bicarbonate solution and saturated brine solution successively. After drying over anhydrous magnesium sulfate, the solvent was evaporated under reduced pressure. The

Table 1

Effect of different catalysts for esterification of mandelic acid with methanol

Entry	Catalyst	Time (h)	Yield (%)[a]
1	PW (5 mol%)	1.5	98
2	PMo (5 mol%)	1.5	90
3	SiO_2 (1 g)	2	5
4	K-10 (1 g)	2	0
5	KSF (1 g)	2	15
6	Activated carbon (1 g)	2	8
7	Γ-Al_2O_3 (1 g)	2	0
8	40% PW/K-10 (5 mol%)	1.5	80
9	40% PW/KSF (5 mol%)	2	40
10	40% PW/γ-Al_2O_3 (5 mol%)	2	53
11	40% PW/C (5 mol%)	2	50
12	40% PMo/SiO_2 (5 mol%)	1	94
13	20% PW/SiO_2 (5 mol%)	2	98
14	60% PW/SiO_2 (5 mol%)	1	98
15	40% PW/SiO_2 (5 mol%)	1	98
16	40% PW/SiO_2 (7 mol%)	1	97
17	40% PW/SiO_2 (2 mol%)	2	96
18	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (20 mol%)	100 (min)	55
19	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (10 mol%)[b]	7 (min)	98
20	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (20 mol%)[b]	3 (min)	98
21	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (30 mol%)[b]	1 (min)	98
22	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (40 mol%)[b]	1 (min)	97
23	TiO_2/SO_4^{2-} [21]	2	96[b]
24	Fe_2SO_4 [20]	3.5	83[b]

[a] Isolated yield.
[b] The reaction performed at reflux condition.

Table 2
Esterification of mandelic acid with alcohols
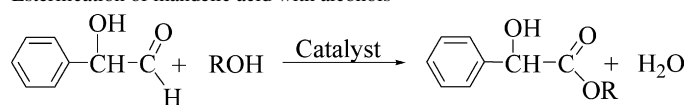
Entry	ROH	Temperature (°C)/time (min)/yield (%)[a]		
		40% PW/SiO$_2$	40% PMo/SiO$_2$	CsPW
1	CH$_3$OH	RT/60/98	RT/65/97	80/1/98
2	C$_2$H$_5$OH	RT/50/97	RT/55/96	80/1/98
3	CH$_3$(CH$_2$)$_3$OH	80/2/98	80/3/97	80/1/97
4	CH$_3$(CH$_2$)$_6$OH	80/2/96	80/3/97	80/1/97
5	CH$_3$(CH$_2$)$_7$OH	80/2/97	80/3/96	80/2/98
6	PhCH$_2$OH	RT/15/98	RT/5/97	RT/15/98
7	Cyclohexanol	80/5/100	80/5/100	80/1/97
8	PhCH$_2$CH$_2$OH	RT/5/95	RT/5/94	80/13/93
9	C$_6$H$_5$OH	80/60/0	80/60/0	80/60/0
10	C$_6$H$_5$SH	80/60/0	80/60/0	80/60/0
11	CH$_3$OH[b]	RT/65/98	RT/65/95	80/2/98
12	CH$_3$OH[b]	RT/70/98	RT/65/91	80/3/91
13	CH$_3$OH[b]	RT/80/98	RT/65/90	80/5/92

[a] Isolated yield.

[b] Reaction with reused catalyst in four successive runs; the catalyst was filtered off, washed with acetonitrile and dried at 150 °C/0.5 Torr for 1.5 h.

crude product was purified by recrystallization from petroleum ether [27].

3. Results and discussion

Initially, esterification of mandelic acid with methanol was performed in the presence of catalytic amount of PW or PMo at room temperature. PW and PMo resulted in good catalytic effects, but PW showed a high yield for this transformation (Table 1, entries 1, 2). The synthesis could not be achieved in the absence of the catalyst, also, all supports showed low reactivity (Table 1, entries 3–7). The acidic salt CsPW, PW/SiO$_2$, PW/K10, PW/KSF, PW/γ-Al$_2$O$_3$, and PW/C were prepared by the literature methods and fully characterized as reported elsewhere [2–7,23]. PW/SiO$_2$ gives the best yield in comparison to other supported catalysts (Table 1, entries 8–12, 15). Although all supports are suitable, SiO$_2$, which is relatively inert towards HPAs, is the one most often used [24].

Then PW/SiO$_2$ with different weight percent of PW to SiO$_2$ was examined, and 40 wt.% PW/SiO$_2$ was chosen (Table 1, entries 13–15). The quantity of catalyst used in this reaction was optimized (Table 1, entries 15–17). The reaction was more efficient in the presence of PW/SiO$_2$ when compared to the

best results of other literature procedure (Table 1, entries 23, 24). More experiments were done with acidic heteropoly salts, CsPW. It showed low reactivity at room temperature (Table 1, entry 18). Thus the reaction was performed at 80 °C, with different percentages of the catalyst loading (Table 1, entries 19–22). Increasing the catalyst from 10 to 30 mol% decreases the time for completion of the reaction. No improvement in yield or time of the reaction was observed when catalyst loading was increased to 40 mol%. The reaction was extended to other primary and secondary alcohols in optimal condition (Table 2). It is noteworthy that cyclohexanol showed lower reactivity than primary alcohols (Table 2, entries 8). In all cases, no side reactions such as etherification, oxidation, elimination, and carbonization were observed.

The primary structures of supported HPAs were identified by comparing their FTIR absorption bands to those of bulk HPAs [25]. FTIR of the supported Keggin HPA catalysts after catalysis preparation and also after catalytic reaction were checked and characteristic peaks were observed. Both catalyst preparation and reaction conditions are mild, thus it is reasonable that the Keggin unit should be intact under the reaction condition. It should be emphasized that some bands were overlapped with those of the supports.

Table 3
Catalyst characterisation

Catalyst[a]	S_{BET}	Pore size (A°)	Pore volume (cm^2/g)	H$_2$O[b] (wt.%)	W[c] (wt.%)
60% PW/SiO$_2$	87	145	0.34	1.8	45.6
40% PW/SiO$_2$	117	227	0.67	4.8	28.9
20% PW/SiO$_2$	208	145	0.75	3.5	15.4
CsPW	125	30	0.095	1.7	61.4

[a] Catalysts pre-treated at 150 °C/0.5 Torr for 1.5 h; PW content from preparation stoichiometry in anhydrous catalysts.

[b] From TGA as a weight loss in the range of 30–300 °C.

[c] W content in anhydrous catalysts from ICP. Typically, the W content from ICP was slightly lower than expected from the preparation stoichiometry.

Due to the high porosity of the catalyst (Table 3), the deposited coke built 7–10 wt.% carbon during the reaction. After reaction, catalysts can be recovered by filtering, washing with acetonitrile and then with acetone. However the catalyst activity were gradually declined, in the case of PW/SiO$_2$ and CsPW time of the reaction increased in successive runs (Table 2, entries 11–13), which indicates loss of catalyst activity probably due to the catalyst coking. UV spectrum test of supernatant portion of PW/SiO$_2$ catalyzed reaction mixture confirmed that a decrease in catalytic activity of 40% PW/SiO$_2$ is not due to the subsequent leaching from the support. A supernatant portion of PW/SiO$_2$ catalyzed reaction mixture did not exhibit an absorption band at around 265 nm assigned to Keggin type PW$_{12}$O$_{40}$$^{3-}$ ions [26]. In order to prove that this system is truly heterogeneous, first the reaction mixture was filtered 30 min after the first run. Then the reaction was resumed with the filtrate, in the absence of any externally added catalyst. No increase in conversion was observed after 2 h, which proves it is a real heterogenic catalyst.

4. Conclusion

In conclusion, the results presented in this paper demonstrate that SiO$_2$ can be regarded as the best support for HPAs in comparison to others. CsPW shows excellent results at 80 °C. PW/SiO$_2$ is an efficient, environmentally friendly, cheap, non-toxic, and reusable catalyst with very easy work-up. Also, the present procedure represents a clean, practical, simple, mild, and time-saving method for synthesis of mandelates with short reaction times and excellent yields with 100% selectivity.

Acknowledgments

References

[1] (a) I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311;
(b) Y. Izumi, K. Urabe, M. Onaka, Zeolite, Clay, and Heteropoly Acid in Organic Reactions, VCH, New York, 1992;
(c) M.R. Torviso, E.N. Alesso, G.Y. Moltrasio, P.G. Vàzquez, L.R. Pizzio, C.V. Càceres, M.N. Blanco, Appl. Catal. A 301 (2006) 25;
(d) T. Okuhara, T. Nishimura, H. Watanabe, M. Misono, J. Mol. Catal. A: Chem. 74 (1992) 247.
[2] L.R. Pizzio, C.V. Càceres, M.N. Blanco, Appl. Catal. A 167 (1998) 283.
[3] P.G. Vàzquez, M.N. Blanco, C.V. Càceres, Catal. Lett. 60 (1999) 205.
[4] L.R. Pizzio, P.G. Vàzquez, C.V. Càceres, M.N. Blanco, Stud. Surf. Sci. Catal. 130 (2000) 953.
[5] L.R. Pizzio, P.G. Vàzquez, A. Kikot, E. Basaldella, C.V. Càceres, M.N. Blanco, Stud. Surf. Sci. Catal. 143 (2002) 739.
[6] E. Caliman, J.A. Dias, S.C.L. Dias, A.G.S. Prado, Catal. Today 816 (2005) 107.
[7] G.D. Yadav, N. Kirthivasan, J. Chem. Soc., Chem. Commun. (1995) 203.
[8] S. Soled, S. Miseo, G. McVicker, W.F. Gates, A. Gutierrez, J. Paes, Catal. Today 36 (1997) 441.
[9] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.
[10] E. Rafiee, F. Shahbazi, J. Mol. Catal. A: Chem. 250 (2006) 57.
[11] (a) E. Rafiee, F. Shahbazi, M. Joshaghani, F. Tork, J. Mol. Catal. A: Chem. 242 (2005) 129;
(b) E. Rafiee, S. Rashidzadeh, A. Azad, J. Mol. Catal. A: Chem. 261 (2006) 49.
[12] F.A. Morton, J.P. Linduska, J. Econ. Entomol. 40 (1947) 562.
[13] B.V. Travis, F.A. Morton, H.A. Jones, J.H. Robinson, J. Econ. Entomol. 42 (1949) 686.
[14] C.N. Smith, D. Burnett, J. Econ. Entomol. 42 (1949) 439.
[15] Piper, Hall, Wright, Ind. Eng. Chem. 43 (1951) 11a.
[16] W.F. Barthel, J. Leon, S.A. Hall, J. Org. Chem. 19 (1954) 485.
[17] S.G. Cohen, R.M. Schultz, S.Y. Weinstein, J. Am. Chem. Soc. 88 (1966) 5315.
[18] R.L. Elsenbaumer, S. Mosher, J. Org. Chem. 44 (1979) 600.
[19] P. Huszthy, J.S. Bradshaw, C.Y. Zhu, R.M. Izatt, J. Org. Chem. 56 (1991) 3330.
[20] G.S. Zhang, H. Gong, Synth. Commun. 29 (1999) 1547.
[21] T.S. Jin, R.Y. Ma, Y. Li, X. Sun, T.S. Li, Synth. Commun. 31 (2001) 2051.
[22] T. Kolasa, M.J. Miller, J. Org. Chem. Rev. 52 (1987) 4978.
[23] E.F. Kozhevnikova, E. Rafiee, I.V. Kozhevnikov, Appl. Catal. A 260 (2004) 25.
[24] I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311 (and references therein).
[25] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, Berlin, 1983, p. 8.
[26] G.D. Yadav, N.S. Asthana, V.S. Kamble, J. Catal. 217 (2003) 88.
[27] Spectroscopic data of products: Methyl mandelate (Table 2, entry 1): M 57–58 °C (reported 58 °C); IR (KBr, cm^{-1}) 3445, 1741; Ethyl mandelate (Table 2, entry 2): M 35–36 °C (reported 37 °C); IR (KBr, cm^{-1}) 3442, 1734; Butyl mandelate (Table 2, entry 3): M 26–27 °C (reported 28 °C); IR (KBr, cm^{-1}) 3440, 1735; Heptyl mandelate (Table 2, entry 4): M Oily (reported oily); IR (KBr, cm^{-1}) 3458, 1724; Octyl madelate (Table 2, entry 5): M Oily (reported oily); IR (KBr, cm^{-1}) 3480, 1730; Benzyl mandelate (Table 2, entry 6): M 92–93 °C (reported 93 °C); IR (KBr, cm^{-1}) 3444, 1741, 1727; Cyclohexyl mandelate (Table 2, entry 7): M 50–51 °C (reported 49–50 °C); IR (KBr, cm^{-1}) 3494, 1723; Phenethyl mandelate (Table 2, entry 8): M 74–75 °C (reported 73–74.5 °C); IR (KBr, cm^{-1}) 3494, 1723.