Applied Catalysis A: General 486 (2014) 55–61

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Regioselective acylation of 2-methoxy naphthalene catalyzed by supported 12-phosphotungstic acid

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ARTICLE INFO

Article history:
Received 18 February 2014
Received in revised form 21 August 2014
Accepted 23 August 2014
Available online 29 August 2014

Keywords:
Naproxen
Acylation
Phosphotungstic acid
Supported
Silica gel
Zirconium sulfate

ABSTRACT

12-Phosphotungstic acid supported on silica gel, zirconium sulfate, and a combination of silica gel and zirconium sulfate (50% w/w) were employed as solid acid catalysts for regioselective acylation of 2-methoxynaphtalene with acetic anhydride. 1-(6-Methoxynaphthalen-2-yl)ethanone (2,6-AMN), a commercially important intermediate for production of Naproxen, was obtained with excellent selectivity (>98%) at 67–68% conversion using 12-phosphotungstic acid supported on silica gel 20% (w/w) in refluxing tetrachloroethane. The unreacted starting material can be easily separated from the product by a simple crystallization from nonane.

1. Introduction

2-(6-Methoxy-naphthalen-2-yl) propanoic acid (**1**) (Naproxen) is a widely used non-steroidal anti-inflammatory agent [1]. The industrial scale synthesis of naproxen involves Friedel-Crafts acylation of 2-methoxynaphthalene (2-MN) (**2**) with acetic anhydride in presence of aluminium chloride to get 1-(6-methoxynaphthalen-2-yl)ethanone (2,6-AMN) (**3**) in the first major step. This step results in a substantial amount of waste and release of HCl which causes corrosion problems [2]. To replace aluminium chloride that acts as a Lewis acid, considerable efforts have been made to explore use of solid acid catalysts such as zeolites, clays, Amberlyst-15, and MCM-41 type silica material [3]. Unfortunately, most of the catalysts yield unwanted 1-(6-methoxynaphthalen-1-yl)ethanone (1,6-AMN) (**4**) as a major product with exception of Zeolite Beta which shows higher selectivity towards the required 2,6-isomer (55%) [4] (Scheme 1).

Several studies have reported application of heteropoly acids (HPAs) for aromatic acylation via Friedel–Crafts reaction [5–21]. For example, benzoylation of veratrole with benzoic anhydride to 3,4-dimethoxy benzophenone using zirconia supported silicotungstic acid has been described by Devassi and Halligudi [19]. Khder and co-workers have used phosphotungstic acid incorporated within mesoporous MCM-41 for Friedel–Crafts acylation of anisole with acetic anhydride [20]. Recently, Chen and co-workers have reported one pot synthesis of 1-acetylpyrene over phosphotungstic acid catalyst supported on oxides such as SiO_2, TiO_2, K-10 montmorillonite and γ-Al_2O_3 with 100% selectivity for 1-acetylpyrene and 91.8% yield on SiO_2-supported phosphotungstic acid [21]. These reports encouraged us to examine acylation of 2-methoxy naphthalene with acetic anhydride catalyzed by supported phosphotungstic acid.

2. Materials and methods

2.1. General

IR spectra were recorded on a Perkin–Elmer RX-1 FT-IR system. HPLC analysis was carried out on Varian Pro Star HPLC unit. Surface area analysis was carried out Quantachrome Instrument, Model-Nova 2000e, surface area and pore size analyzer, with Autosorb software, USA. X-ray diffraction (XRD) patterns were obtained on

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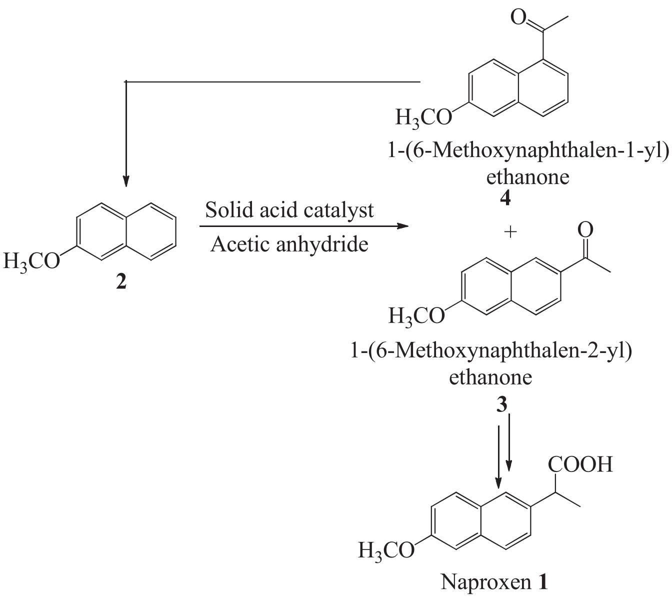
http://dx.doi.org/10.1016/j.apcata.2014.08.026



Scheme 1. Acylation of 2-methoxy naphthalene.

Seimens D 5000 (Cheshire, UK) X-ray diffractometer over a 2θ range of 2–65° using $CuK_{\alpha1}$ radiation (0.15406 nm). X-ray photoemission spectroscopy (XPS) analyses of catalysts were performed on a VG Scientific ESCA-3000 spectrometer using a non-monochromatized Mg Kα radiation (1253.6 eV). Binding energies (BE) were referenced with the C1S line corresponding at 284.6 eV with an accuracy of ~0.1 eV for the XPS analysis. Raman spectra were recorded on a Horiba Jobin-Yvon LabRam HR 800 UV Raman spectrometer with a 35 mW internal He-Ne laser source of excitation wavelength 514 nm. The TEM images were obtained on a Tecnai (model-F20) 120 kV field emission gun with tungsten filament as an electron generator source. The samples for TEM were prepared by dispersing the synthesized catalysts in isopropanol and drop casted over 200 mesh size carbon-coated copper TEM grids.

2-Methoxy naphthalene (**2**) and authentic samples of 1-(6-methoxynaphthalen-2-yl)ethanone (**3**) and 1-(6-methoxynaphthalen-1-yl)ethanone (**4**) were a generous gift from M/s Godavari Drugs, Hyderabad. 12-Phosphotungstic acid hydrate (H_3PW) Cat. No. 40116 and zirconium IV sulphate tetrahydrate Cat. No. 41041 (ZS) were obtained from Alfa Aesar, Hyderabad, India. Silica gel for column chromatography 60–120 mesh (SG) was obtained from ACME Synthetic Chemicals, Mumbai, India. All other reagents and solvents were of analytical grade obtained from Qualigens, India.

2.2. Preparation of supported catalysts

Supported H_3PW catalysts were prepared by stirring the support (10 g) with an aqueous solution of H_3PW (100 mL). The mixture was stirred for 6 h at room temperature followed by drying on a rotary evaporator. Finally, the catalyst was dried by heating at 140 °C under vacuum (2 mmHg pressure) for 3 h.

2.3. Surface area measurement

Surface areas were measured using multi point BET nitrogen adsorption method. Weighed amounts of samples were placed in glass cells and degassed under reduced pressure with nitrogen at 60 °C for 3 h. After degassing, the samples cells were immersed in liquid nitrogen at −196 °C, and total surface area was obtained from the volume of nitrogen (cm^3/g) adsorbed onto the surface as a function of relative pressure. Total surface area was calculated by multipoint BET method.

2.4. Acylation reaction

2-Methoxy naphthalene **2** (1 g, 0.01 mol) and acetic anhydride (0.66 mL, 0.015 mol) were dissolved in the solvent (10 mL), the catalyst was added and the contents were refluxed for 3 h. After cooling to room temperature, the catalyst was filtered off and washed with the solvent. The solvent from combined washings was removed under reduced pressure and the crude product was analyzed by HPLC. The products were identified from NMR and their retention times in HPLC analysis. Conversion and product selectivity was determined from their respective concentrations in the crude mixture based on their peak areas and corresponding response factors.

2.5. HPLC analysis

Formation of **3** and **4** by acylation of **2** was monitored by reverse phase HPLC. Column C-8 (250 × 5 mm), Chrompack, The Netherlands. Mobile phase, 50% CH_3CN–water. Flow rate, 0.7 mL/min. Detection wavelength, 254 nm. Retention times: 1-(6-methoxynaphthalen-2-yl)ethanone (**3**): 16.79 min; 1-(6-Methoxy-2-naphthyl)-1-ethanone (**4**): 17.87 min; 2-Methoxy naphthalene (**2**): 24.21 min.

2.6. Separation of 2,6-AMN and 2-MN

The combined product of 5 runs (5 g) consisting of 60:40 mixture of 2,6-AMN and 2-MN was dissolved in hot nonane (50 mL), heated to 80 °C to obtain a clear solution and slowly cooled to 20 °C. 2,6-AMN crystallized out as white crystals. These were filtered, washed once with nonane (5 mL) and dried under vacuum at 50 °C. Yield (2.9 g, 96.6%) with 99% purity. The filtrate was concentrated under reduced pressure to obtain unreacted 2-MN (1.95 g, 97.5%, purity 95% (HPLC).

3. Results and discussion

3.1. Catalyst characterization

3.1.1. FT-IR spectra

In FT-IR spectra, unsupported catalyst shows typical bands for absorptions of P–O (1080 cm^{-1}), $W{=}O_t$ (983 cm^{-1}), $W{-}O_c{-}W$ (898 cm^{-1}) and $W{-}O_e{-}W$ (797 cm^{-1}). These bands are preserved on the supported samples, but they are broadened and partly obscured because of the strong absorption of supports. These observations are similar to those reported by Dias and co-workers [11].

3.1.2. XRD analysis

XRD patterns were obtained to confirm that H_3PW was effectively supported on SG and ZS-SG. Unsupported H_3PW exhibits sharp and narrow diffraction lines (Fig. 1b). In case of silica gel supported catalyst, the diffraction lines are not very prominent due to strong binding of the catalyst. In case of H_3PW supported on ZS-SG prepared by heating at 140 °C, the diffraction lines can be observed, although with less intensities (Fig. 1c). These lines are also seen in case of supported ZS-SG catalyst recovered after the acylation reaction (Fig. 1d), and washing with CH_2Cl_2 (Fig. 1e). The pattern is still visible in case of catalyst calcined at 300 °C (Fig. 2a) for removal of soft coke, and is completely lost when it is calcined at 400 °C in our attempts to remove the hard coke (Fig. 2b). These observations indicate that H_3PW has a strong interaction and good dispersion on the support which is destroyed if heated beyond 370 °C.

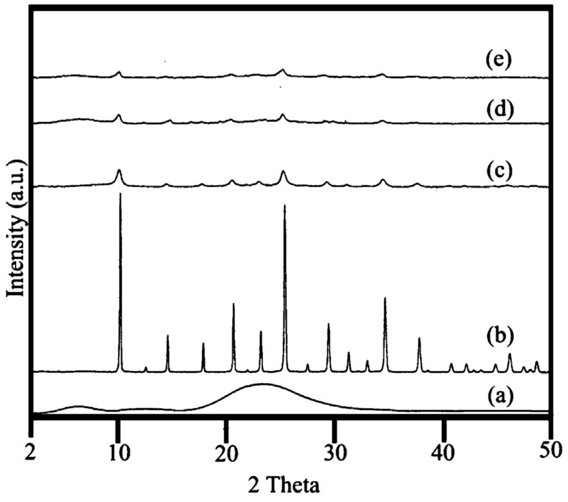


Fig. 1. XRD patterns of (a) Zs-SG support, (b) unsupported H_3PW, (c) 20% (w/w) H_3PW/Zs-SG, (d) catalyst recovered after filtration, (e) recovered catalyst after washing with dichloromethane.

3.1.3. *Surface acidity*

Changes in surface acidity of the catalysts were followed by temperature programmed desorption (TPD) of ammonia (Table 2). Since the Keggin structure of H_3PW is lost above 400 °C [10], we have studied the changes below 400 °C where weak and moderate acidities can be measured. The catalyst with 20% loading of H_3PW on silica has acidity of 14.5 mL/g, mainly due to weak acidic sites. Combining ZS with SG for supporting H_3PW increases the medium acidic sites of the samples and total acidity of the sample also increases (13.1 mL/g). A minor decrease in total acidity was observed for the spent samples most probably due to deposition non-removable hard coke.

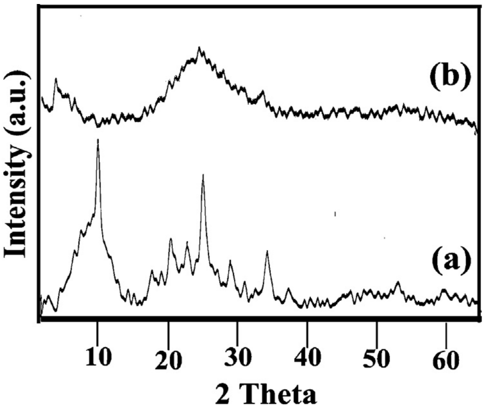


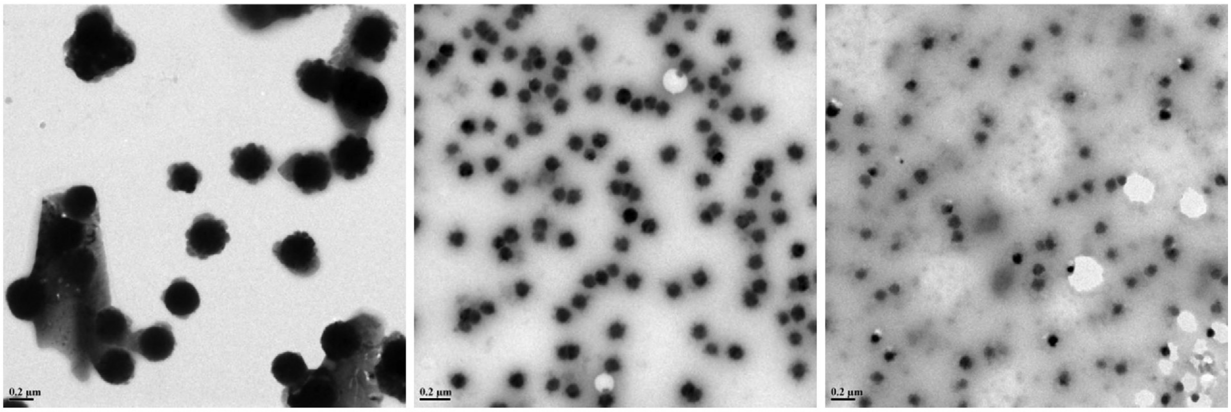
Fig. 2. XRD patterns of 20% (w/w) H_3PW on ZS-SG. (a) Calcination at 300 °C, (b) calcination at 400 °C.

3.1.4. *Surface area measurement*

The crystalline materials, zirconium sulphate and H_3PW have very low surface areas (≈2 m^2/g). Silica gel support has a large surface area (411 m^2/g) which decreases to 279 m^2/g after loading of H_3PW due coverage of the surface by the catalyst. In a similar fashion, deposition of zirconium sulphate on silica gel reduces the surface area of ZS-SG catalyst to 120 m^2/g. Loading of H_3PW on this catalyst causes a further decrease to 94 m^2/g (Table 2). However, the surface areas do not change significantly after acylation reaction and washing with dichloromethane indicating that H_3PW is retained in these supports.

3.1.5. *Transmission electron microscopy*

The surface morphology of the catalyst H_3PW supported on ZS-SG was probed by transmission electron microscopy (TEM). The unsupported catalyst (Fig. 3a) appears to be polydispersed with



(a) (b) (c)

Fig. 3. Representative TEM images of the catalysts. (a) Unsupported H_3PW; (b) H_3PW (20% w/w) supported on ZS-SG after reaction; (c) H_3PW (20% w/w) supported on ZS-SG after reaction and DCM wash.

Table 1
Phosphotungstic acid catalyzed acylation of 2-methoxynaphthalene with acetic anhydride in different solvents[a].

Entry	Solvent	Temperature (°C)	Conversion	2,6-isomer (**3**) (%)	1,6-isomer (**4**) (%)
1.	Acetonitrile	60	84	15	69
2.	Dichloromethane	60	55	7	48
3.	Dichloroethane	84	62	20	42
4.	Tetrachloroethane	140	78	22	56
5.	Nitrobenzene[b]	140	90	38	8
6.	N-Methylpyrrolidinone	140	No reaction		

[a] 2-Methoxynaphthalene (6.3 mmol), acetic anhydride 0.71 g, 7 mmol, catalyst 182 mg (1 mol%), 10 mL solvent, reaction period 3 h.
[b] Reaction accompanied by tar formation.

Table 2
Acylation of 2-methoxynaphthalene with various catalysts[a].

Support	H_3PW loading (%, w/w)	Surface area (m^2/g)	Total acidity (mL/g)	Conversion (%)	2,6-AMN Selectivity (%)
H_3PW	100	2.12		78	28
SG	0	411	0	0	0
	10	nd[b]	nd	47	85.6
	20	279	14.5	68	98.3
	30	nd	nd	46	88.6
ZS	0	2.60	nd	0	0
	10	nd	nd	12	91.1
	20	1.06	25.5	47	97.5
	30	nd	nd	7	84.3
ZS-SG (1:1 w/w)	0	120	nd	0	0
	10	nd	nd	56	97.5
	20	94	13.1	67	98.3
	30	nd	nd	39	97.0

[a] 2-Methoxynaphthalene (1 g, 6.3 mmol), acetic anhydride (0.71 g, 7 mmol), catalyst (1 g), solvent (10 mL), reaction period 3 h at 140 °C in tetrachloroethane.

[b] nd: Not determined.

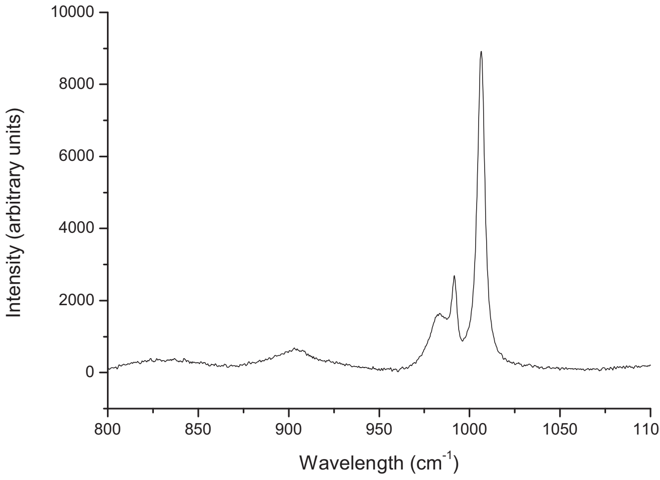


Fig. 4. Raman spectrum of unsupported H_3PW.

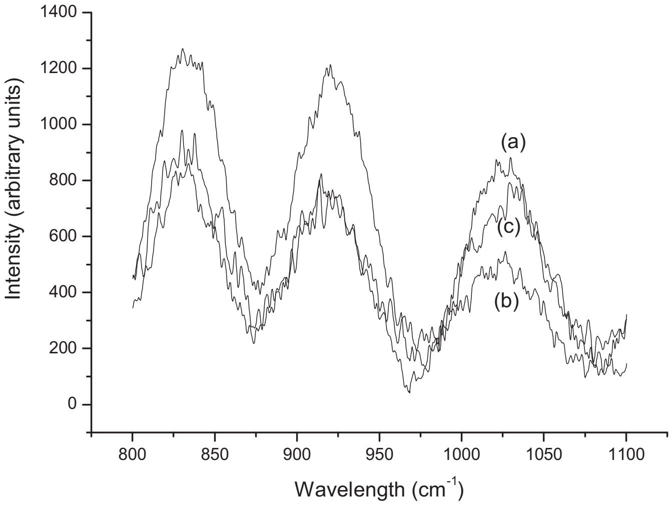


Fig. 5. Raman spectra of 20% (w/w) H_3PW supported on ZS-SG (a) before reaction; (b) after reaction; and (c) after DCM wash.

rounded shape. The morphology of supported catalyst particles shows that the catalyst particles are uniformly distributed in the ZS-SG matrix. The morphology does not change significantly after the reaction (Fig. 3b), and also after washing with dicholoromethane (Fig. 3c).

3.2. Raman spectra

Pure H_3PW shows a sharp band at 1006 cm^{-1} with shoulders at 992 and 983 cm^{-1} (Fig. 4). The bands at 1006 and 992 cm^{-1} can be attributed to ν(W═O) symmetric and asymmetric stretching modes while the band observed at 983 cm^{-1} can be assigned to the ν(W–O–W) asymmetric stretching mode. After being supported on ZS-SG, the position of ν(W═O) band at 1006 cm^{-1} is shifted to 1026 cm^{-1} indicating an increased interaction with the support. The bands at 833 cm^{-1} and 920 cm^{-1} are most probably due to ν(W–O–Zr) vibration and ν(W–O–W) stretching mode, respectively (Fig. 5a) [19,22–24]. Interestingly, the recovered supported catalyst shows a small decrease in the intensity of the peaks (Fig. 5b), which is partly recovered after washing with dichloromethane (Fig. 5c).

3.2.1. X-ray photoemission spectroscopy (XPS)

In Fig. 6a, XPS spectrum of 20% (w/w) H_3PW on SG clearly shows peak of W $4f_{7/2}$ appearing at 39.8 eV. Normally, this peak in XPS appears around 36–36.3 eV [24]. If there are more electronegative atoms in the vicinity of tungsten, the binding energy values shift towards the high end. After the acylation reaction, the binding energy peak of $4f_{7/2}$ electron of W appears at 38.2 eV which is slightly deviated from that of the catalysts peak (Fig. 6 b). From the XPS data it is confirmed that catalysts contains the W atoms and there is no change in its electronic state as expected for a Lewis acid catalyzed acylation reaction which does not involve electron transfer.

3.3. Solvent effects on acylation reaction

Initially, the acylation of 2-methoxy naphthalene with acetic anhydride using unsupported phosphotungstic acid as catalyst (surface area 2.12 m^2/g) was carried out in different solvents at their reflux temperatures (Table 1). Tetrachloroethane was found to be the most appropriate solvent. It is a neutral solvent having good dielectric constant (7.096) and is reported to be capable of showing specific interactions with aromatic hydrocarbons [25]. Also, the boiling point (140 °C) is high enough to carry out the reaction at a fair rate and solvent recovery is highly efficient (>97%). Our findings are in agreement with Chen and co-workers [21] and further studies were made using tetrachloroethane as the solvent.

3.4. Effect of temperature

The acylation reaction catalyzed by H_3PW was studied at temperatures ranging from 30 °C to 140 °C. Surprisingly, acylation

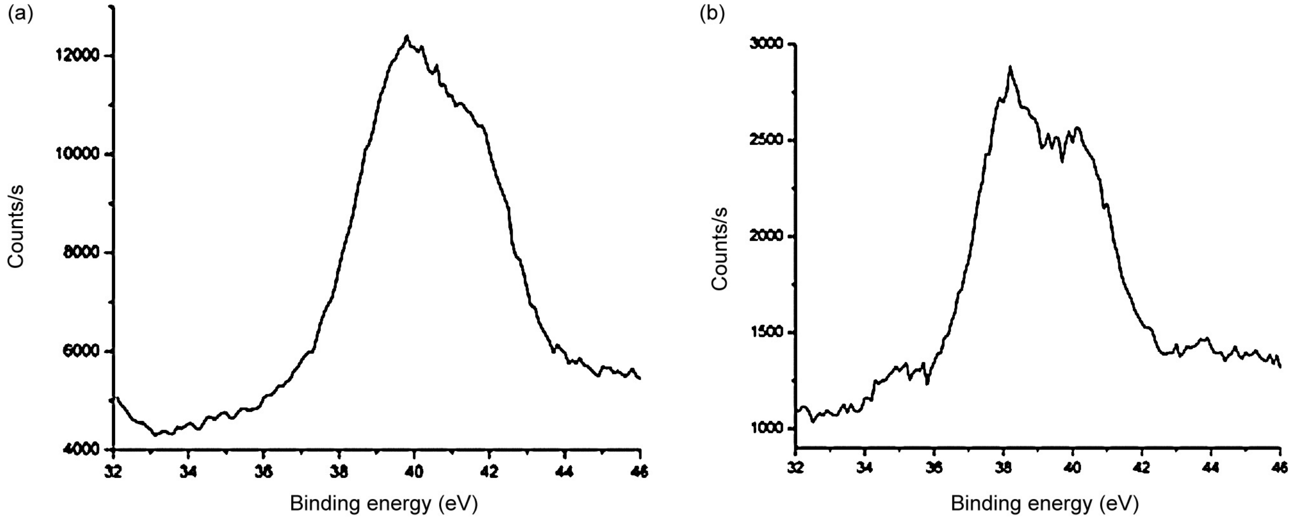


Fig. 6. (a) XPS of 20% (w/w) H_3PW supported on SG (before reaction). (b) XPS of 20% (w/w) H_3PW supported on SG (after reaction).

reaction took place even at room temperature with 70% conversion in 3 h. By increasing temperature to 140 °C, the conversion increased only to 80% but selectivity towards formation of 2,6-AMN increased dramatically (Fig. 7). This increased selectivity with increasing temperature is most probably due to comparative instability of the 1,6-isomer which deacylates to 2-methoxynaphthalene at higher temperatures (Scheme 1) while the 2,6-isomer remains unaffected [12].

3.5. *Acylation with supported H_3PW*

Kukovecz and co-workers have demonstrated the presence of Lewis acid sites in silica supports [13] which are essential for Friedel-Crafts alkylation and acylation reactions. It occurred to us that introduction of extra Lewis acid sites might further improve the selectivity in H_3PW catalyzed acylation of 2-MN. We have hence carried out acylation reactions using phosphotungstic acid (H_3PW) supported on various supports (10% w/w) such as zirconium sulfate (ZS), and silica gel (SG). A combination of 50% (w/w) zirconium sulfate and silica gel (ZS–SG) was also tried. Control reactions were carried out using basic and neutral alumina, pure zirconium sulfate and silica gel without H_3PW (Table 2). Since it is well established that H_3PW loses its Keggin structure at high temperatures [10,14], all catalysts were prepared by heating at 140 °C under vacuum.

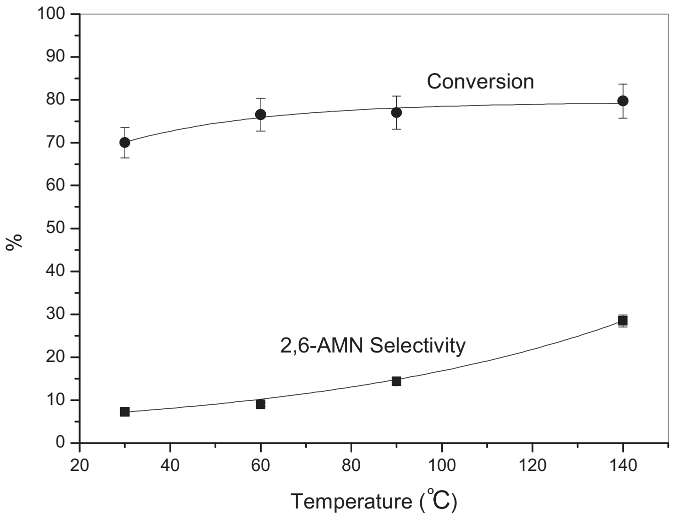


Fig. 7. Effect of temperature on conversion and selectivity towards formation of 2,6-AMN during acylation of 2-methoxy naphthalene catalyzed by H_3PW in tetrachloroethane. 2-Methoxynaphthalene (1 g, 6.3 mmol), acetic anhydride (0.71 g, 7 mmol), catalyst (182 mg, 1 mol%), 10 mL solvent, reaction period 3 h.

The results in Table 2 show that supporting the heteropoly acid on another support bearing Lewis acid sites does result in steering the selectivity towards the required 2,6-AMN. It was confirmed from control experiments that the supports without H_3PW (neutral and basic alumina, silica gel and zirconium sulfate) did not catalyze the acylation reaction.

3.6. *Effect of H_3PW loading*

In order to optimize the catalyst loading, further studies were carried out by varying the amount of loading of the catalyst on supports from 10 to 30% (Table 2). In all the three cases, both selectivity and conversion increased on increasing catalyst loading from 10 to 20% (w/w) but further increase in catalyst loading to 30% caused a drop in both selectivity and conversion. This can be understood as follows: as the concentration of H_3PW on support increases, the synergistic action of the Lewis acidic sites of supports and H_3PW produces more and more 2,6-AMN. This reaches maximum at 20% loading. Further increase in H_3PW loading causes the catalyst to start resembling unsupported H_3PW and the selectivity starts dropping. This is further supported by the observation that increasing the amount of supported catalyst (20% H_3PW on silica gel) in the reaction flask from 500 mg to 1 g at fixed amounts of reactants, the conversion remains unchanged at 68 (±2%) while the selectivity increases from 85% to 98% (Fig. 8).

3.7. *Time course of reaction*

The course of acylation reaction in presence of supported catalysts with 20% (w/w) H3PW loading was studied to optimize the reaction conditions further. In all the three cases, the reaction reached maximum conversion in 3 h with 98% selectivity (Fig. 9).

Continuing the reaction for longer period caused the product to decompose and produce 2-methoxynaphthalene. This was glaringly obvious in case of H_3PW-ZS catalyst where whole of 2-methoxy naphthalene was recovered after an overnight reaction.

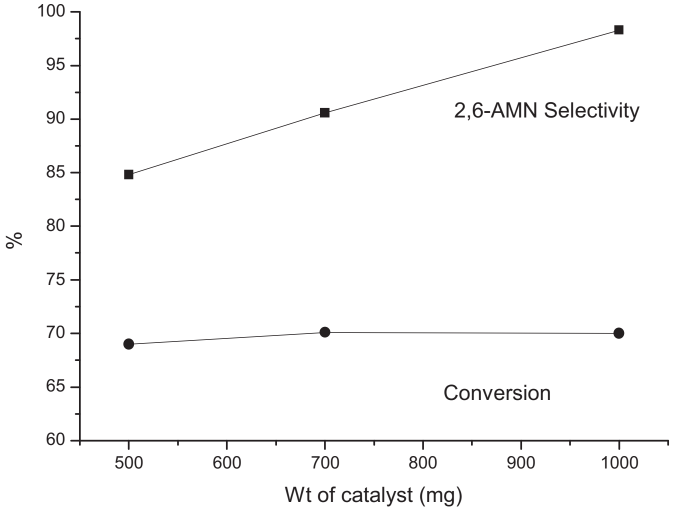


Fig. 8. Effect of catalyst amount on acylation. 2-Methoxynaphthalene (1 g, 6.3 mmol), acetic anhydride (0.71 g, 7 mmol), solvent (10 mL). Temp. 140 °C. Reaction period 3 h.

3.8. *Reusability of the catalyst*

Reusability of the catalyst was studied for both SG and ZS-SG supports. Reaction was carried out under standardized conditions (2-MN, 1 g; Ac_2O, 0.71 g; catalyst, 1 g; tetrachloroethane, 10 mL, temp. 140 °C; reaction period 3 h). After the reaction, the product was filtered, the catalyst was washed with dichloromethane to remove soft coke [10,14] and reused. Silica gel supported catalyst could be used twice with full activity which decreases by 30% in the third cycle. In comparison, the ZS-Silica supported catalyst loses 70% of its activity after a single use (Fig. 10).

Observed deactivation of the catalyst is most probably due to formation of coke. The extraction with CH_2Cl_2 removes soft coke but not the hard coke. This was also evident from the increasing dark brown colour of the catalyst after each recycle. We have tried to remove the hard coke by aerobic treatment at high temperatures (500–550 °C) [10]. However, such a treatment did not lead to recovery of catalytic activity. Kozhevnikov et al. have reported that H_3PW decomposes and loses its Keggin structure when heated beyond 370 °C [10] and this is probably the reason for loss of catalytic activity. XRD data support this possibility. Fig. 2a shows the presence of characteristic peaks in XRD patterns of H_3PW supported on ZS-SG calcined at 300 °C which are lost when the catalyst is calcined at 400 °C (Fig. 2b). Coking and regeneration of the H_3PW supported on Si has been well studied by Kozhevnikov et al. [14] and we are currently exploring the different possibilities of catalyst regeneration for the acylation reaction.

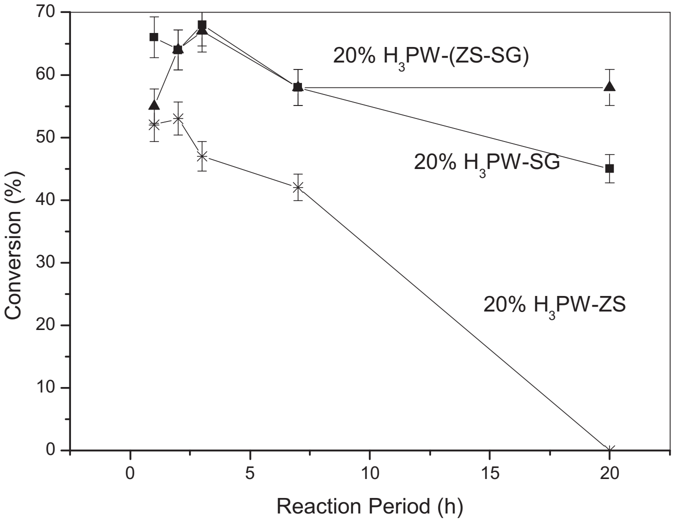


Fig. 9. Time course of the reaction. 2-Methoxynaphthalene (1 g, 6.3 mmol), acetic anhydride (0.71 g, 7 mmol), catalyst (1 g), solvent (10 mL). Temp. 140 °C.

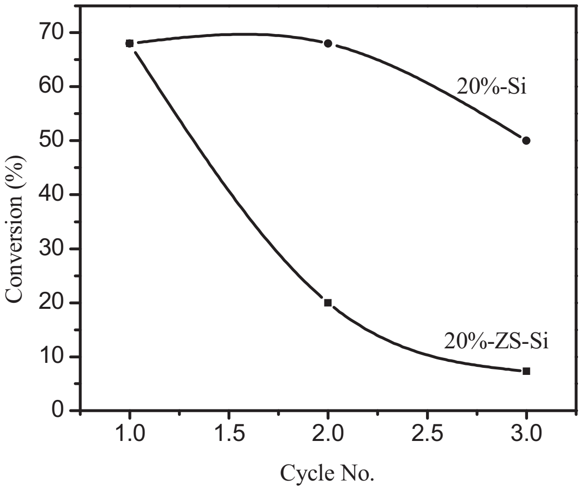


Fig. 10. Reusability of the catalyst.

4. Conclusion

Selectivity in acylation of 2-methoxy naphthalene catalyzed by heteropoly acid, 12-phosphotungstic acid, was studied. The catalyst was supported on silica gel, zirconium sulfate and a combination of silica gel and zirconium sulfate. Effects of catalyst loading, temperature, solvent and reaction period on selectivity towards formation of commercially important intermediate 2,6-AMN was studied in detail. The best catalyst was found to be 20% (w/w) 12-phosphotungstic acid supported on silica gel. Under optimum conditions, the catalyst shows excellent selectivity (>98%) at 67–68% conversion. The unreacted starting material can be easily separated from product by a simple crystallization from nonane and reused.

Acknowledgement

We thank CSIR New Delhi for financial support under XII 5 year plan CSC0108-ORIGIN, and Prof. Dr V Vishwanathan, Sreyas Institute of Engineering and Technology, Hyderabad for helpful discussions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.08.026.

References

[1] (a) I.T. Harrison, B. Lewis, P. Nelson, W. Rooks, A. Roszkowoski, A. Tomolonis, J.H. Fried, J. Med. Chem. 13 (1970) 203–205;
(b) J. Riegl, M.L. Maddox, I.T. Harrison, J. Med. Chem. 17 (1974) 377–378;
(c) C. Giordano, G. Castaldi, F. Uggeri, Angew. Chem., Int. Ed. Engl. 23 (1984) 413–419;
(d) Q.-M. Gu, C.-S. Chen, Tetrahedron Lett. 27 (1986) 1763–1766;
(e) C. Giordano, G. Castaldi, S. Cavicchioli, M. Villa, Tetrahedron 45 (1989) 4243–4252;

(f) H.R. Sonawane, N.S. Bellur, J.R. Ahuja, D.G. Kulkarni, Tetrahedron: Asymmetry 3 (1992) 163–192;
(g) T. Manimaran, P. Stahly, Tetrahedron: Asymmetry 4 (1993) 1949–1954;
(h) W.-C. Huang, S.-W. Tsai, C.-S. Chang, J. Chin. Inst. Chem. Eng. 29 (1998) 153–159.

[2] G.A. Olah, Friedel–Crafts and Related Reactions, Wiley–Interscience, New York, 1973.

[3] H. Szmant, Organic Building Blocks of the Industrial Industry, Wiley, New York, 1989, pp. 504.

[4] D. Rohan, C. Canaff, E. Fromentin, M. Guisnet, J. Catal. 177 (1998) 296–305.

[5] P. Gupta, S. Paul, Catalysis Today (2014), doi.org/10.1016/j.cattod.2014.04.010.

[6] S.E. Collins, S.R. Matkovic, A.L. Bonivardi, L.E. Briand, J. Phys. Chem. C 115 (2011) 700–709.

[7] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113–252.

[8] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.

[9] C. Castro, J. Primo, A. Corma, J. Mol. Catal. A: Chem. 134 (1998) 215–222.

[10] J. Kaur, K. Griffin, B. Harrison, I.V. Kozhevnikov, J. Catal. 20 (2002) 448–455.

[11] J.A. Dias, E. Caliman, S.C.L. Dias, M. Paulo, A.T.C.P. de Souza, Catal. Today 85 (2003) 39–48.

[12] R.V. Jasra, Bull. Catal. Soc. India 2 (2003) 157–183.

[13] A. Kukovecz, Zs. Balogi, Z. Konya, M. Toba, P. Lentz, S.-I. Niwa, F. Mizukami, A. Molnar, B.J. Nagy, I. Kiricsi, Appl. Catal. A 228 (2002) 83–94.

[14] I.V. Kozhevnikov, S. Holmes, M.R.H. Siddiqui, Appl. Catal. A 214 (2001) 47–58.

[15] T. Tagawa, J. Amemiya, S. Goto, Appl. Catal. A 257 (2004) 19–23.

[16] J. Kaur, K. Griffin, B. Harrison, I.V. Kozhevnikov, J. Catal. 208 (2002) 448–455.

[17] H. Firouzabadi, N. Iranpoor, F. Nowrouzi, Tetrahedron 60 (2004) 10843–10850.

[18] M. Chen, D. Li, Y. Luo, M.Q. He, J.M. Xie, H.M. Li, X.H. Yuan, J. Ind. Eng. Chem. 17 (2011) 14–17.

[19] M. Biju, S.B. Devassy, Halligudi, J. Catal. 236 (2005) 313–323.

[20] A.E.R.S. Khder, H.M.A. Hassan, M.S. El-Shall, Appl. Catal. A 411–412 (2012) 77–86.

[21] M.-Q. He, A.-X. Pan, J.-M. Xie, D.-L. Jiang, X.-H. Yuan, M. Chen, Reac. Kinet. Mech. Cat. 108 (2013) 531–544.

[22] C.M. Teague, X. Li, M.E. Biggin, L. Lee, J. Kim, A.A. Gewirth, J. Phys. Chem. B 108 (2004) 1974–1985.

[23] S. Loridant, C. Feche, N. Essayem, F. Figueras, J. Phys. Chem. B 109 (2005) 5631–5637.

[24] N. Legagneux, J.M. Basset, A. Thomas, F. Lefebvre, A. Goguet, J. Sa, C. Hardacre, Dalton Trans. (2009) 2235–2240.

[25] N. Jagan, A.D. Tripathi, J. Chem. Soc., Faraday Trans. 1 (80) (1984) 1517–1524.