



Secondary alcohols oxidation with hydrogen peroxide catalyzed by $[n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_3\text{PW}_{12}\text{O}_{40}$: Transform-and-retransform process between catalytic precursor and catalytic activity species

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ABSTRACT

$[n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_3\text{PW}_{12}\text{O}_{40}$ (**1a**) catalyzed the oxidation of secondary alcohols with 27.5% aqueous hydrogen peroxide under solvent-free conditions. The isolated yields of all ketones were higher than 92%. The turnover number of the catalyst **1a** was above 368, and the highest TON and TOF were up to 3840 and 320 h⁻¹. In this catalytic system, the catalytic active species was $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$, which was formed from **1a** in the reaction. It was discovered that $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ (PW₄) and $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (PW₁₂) kept an equilibrium during the alcohol oxidation by simultaneous monitoring the distribution of species in organic and aqueous phases. The analysis of the W content in the aqueous phase by ICP and the detection of the species transformation in the organic phase by ³¹P NMR revealed that the most of the PW₄ species were transformed to the PW₁₂ species again after the reaction. PW₁₂ and PW₄ were in the transform-and-retransform process.

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1. Introduction

The oxidation of alcohols into the corresponding carbonyl compounds is one of the most vital functional group transformations in organic synthesis [1]. Many traditional inorganic oxidants for alcohols oxidation are well known [2], such as PCC, MnO₂, Na₂Cr₂O₇, NaClO, KMnO₄; however, usually these reagents are hazardous or toxic. Due to the economic and environmental viewpoints, the quest for developing the clean and atom economy [3] catalytic oxidation process for converting alcohols to carbonyl compounds on an industrial scale which employs safer and inexpensive oxidants, such as molecular oxygen or hydrogen peroxide, remains an important challenge.

Molecular oxygen is obviously the cheapest and ideal oxidant. A great deal of results [4] was reported on alcohol oxidation with oxygen as an oxidant, such as Sheldon's PhenS-Pd(OAc)₂ and CuBr₂/TEMPO/Bipy/*t*-BuOK, Ragauskas's acetamido-TEMPO/Cu(ClO₄)₂/TMDP/DABCO and VO(acac)₂/DABCO-

[BMIM]PF₆, Neumann's H₅[PV₂Mo₁₀O₄₀], Ishii's NHPI/Co(Ac)₂, Hu's NaNO₂/Br₂/TEMPO and Wang's Pd/Al₂O₃ and so on. Excellent yields of carbonyl compounds were obtained in these systems under mild conditions. Hydrogen peroxide is also a very attractive and clean oxidant for liquid-phase oxidation. Besides water as the sole byproduct, it provides a high content of active oxygen species and is much cheaper and safer than organic peroxides or peracids [5]. Recently, the catalytic oxidation of alcohols using hydrogen peroxide has received much attention from the viewpoint of green chemistry. Most examples of alcohol oxidation employed polyoxometalates (POM) [6] as catalysts and hydrogen peroxide as an oxidant. For example, $[\pi\text{-C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PW}_{12}\text{O}_{40}$, $[\pi\text{-C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PMo}_{12}\text{O}_{40}$, $[n\text{-}(\text{C}_8\text{H}_{17})_3\text{NCH}_3]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$, $[n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_3[\text{PW}_4\text{O}_{16}]$, Na₁₂[WZnZn₂(H₂O)₂(ZnW₉O₃₄)₂], [BMIM]₃{PO₄[WO(O₂)₂]₄}-[BMIM]PF₆, $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$, Na₆[SiW₁₁ZnH₂O₄₀]-12H₂O and $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ were shown to catalyze the oxidation of alcohol with hydrogen peroxide as a primary oxidant.

During the POM catalytic oxidation, mostly active oxygen species were firstly formed from H₂O₂ by reacting with the catalyst and then oxidized alcohols. The 12-phosphotungstate catalyst with the Keggin structure is a kind of Venturolo-Ishii catalyst

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which was successfully applied to the catalytic alkene epoxidation [6a,7]. It was proved that PW_{12} was first degraded to PW_4 by excess hydrogen peroxide, and that PW_4 was the active species in the Venturello–Ishii catalytic system [8]. Meanwhile, PW_{12} could also be applied to the catalytic alcohols oxidation [6a]. Ikegami and co workers developed a new recyclable catalytic system comprising 12-phosphotungstic acid and a temperature-responsive polymer support and used it for the catalytic alcohol oxidation; the recovered catalyst was unchanged and no other species were evident [9]. The fact that PW_{12} just formed PW_4 in the hydrogen peroxide oxidation reaction was reported in literature [8], but they did not mention that PW_4 could be transformed to PW_{12} , and did not expatiate on the transforming relationship between PW_4 and PW_{12} , especially in alcohol oxidation.

Here we present an environment-friendly and efficient procedure for the secondary alcohol oxidation catalyzed by $[n-C_{16}H_{33}N(CH_3)_3]_3PW_{12}O_{40}$ using 27.5% aqueous hydrogen peroxide under solvent-free conditions. Ketone was produced satisfactorily from secondary alcohol oxidation with high TON and TOF. In this catalytic system, ^{31}P NMR spectra and ICP data showed that PW_{12} was partially degraded to PW_4 by its reaction with H_2O_2 , and the residual PW_{12} and PW_4 were in equilibrium during the oxidation process. Meanwhile, it was found that PW_4 was transformed to PW_{12} again after the reaction. The novel transform-and-retransform process was first discovered between PW_{12} and PW_4 in the alcohol oxidation, which was different from the oxidation process using PW_{12} as a catalyst reported previously. The transforming relationship between PW_4 and PW_{12} was elaborated in this work.

2. Experimental

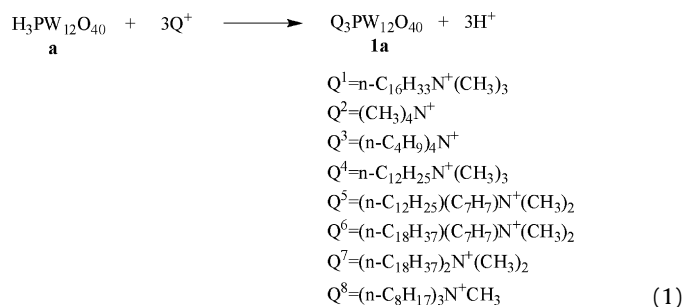
2.1. General

GC analysis was performed by an Agilent 6820 gas chromatograph with an FID detector equipped with a $2\text{ m} \times 2\text{ mm}$ id. 10%QF-1 80–100 mesh Chromosorb WHP stainless steel packed column. The ^{31}P NMR spectra were recorded at 9.4 T by a Bruker DRX 400 spectrometer. The ^{31}P MAS NMR spectra of solid catalyst with high-power proton decoupling were performed at 161.9 MHz by BBO MAS probe head using 4 mm ZrO_2 rotors, 2.0 μs pulse, 2 s repetition time and 2048 scans, with samples spun at 8 kHz and referenced to 85% H_3PO_4 . The ^{31}P NMR spectra of the catalysts in solvents were obtained by a BBI 5 mm converse phase broadband probe head using real sample solution with D_2O internal tube locking field. The IR spectra were carried out on a Bruker TENSOR 27 FTIR spectrometer in a transmission mode (32 scans, 1 cm^{-1} resolution) with a KBr pellet, and OPUS software (Version 4.0) was used for spectra acquisition and processing. Commercially available organic and inorganic compounds were used without further purification.

2.2. Preparation of catalysts **1a–8a**

A solution of 12-phosphotungstic acid (4.32 g, 1.5 mmol) in distilled water (20 ml) was added dropwise to a solution of corresponding alkyl ammonium chloride (4.5 mmol) in distilled water (80 ml) while stirring vigorously (Eq. (1)). The solution of 1:1(v/v) acetone and distilled water was used to dissolve the alkyl ammonium chloride during the preparation of **6a**, **7a** and **8a**. The white precipitate of alkylammonium 12-phosphotungstate appeared immediately, and then the suspended solution continued to be stirred for 1 h. The white precipitate was filtered, washed with

distilled water twice, and dried 24 h under low pressure.



2.3. General procedure for oxidation of alcohols

Reactions were carried out in a 70 ml closed pressure glass tube equipped with magnetic stirring at $363 \pm 0.5\text{ K}$ for about 6–12 h. The alcohol, hydrogen peroxide (27.5%) and catalyst were in a corresponding ratio. The reaction solution was sampled and analyzed by GC using an internal standard technique, and the yield was based on hydrogen peroxide. In the large-scale (500 mmol) reaction, the reaction was carried out in a three-neck round-bottom flask and hydrogen peroxide was added dropwise to the alcohol under refluxing. The products were identified by comparison of their mass and NMR spectra with those of authentic samples. The catalyst was precipitated and recovered by adding diethyl ether into the reactor after the reaction. After the precipitation was completed, the recovered **1a** was separated by centrifugation and reused after washed by diethyl ether and dried under air.

3. Results and discussion

3.1. Preparation and characterization of the catalysts

A series of catalysts (**1a–8a**) was synthesized by mixing 12-phosphotungstic acid with three equivalents of various ammonium cations in water at room temperature for 1 h. All the desired catalysts were precipitated immediately after mixing phosphotungstic acid and ammonium cations because of the poor solubility in water. Then the insoluble catalysts were washed with distilled water and dried in a vacuum drier. These catalysts were characterized by ^{31}P NMR (Fig. 1) and IR (Fig. 2) spectra, respectively. The ^{31}P NMR spectra of **1a–8a** in DMF showed a signal peak at $\delta = -14.5\text{ ppm}$ which corresponds to the ^{31}P NMR chemical shift of the 12-phosphotungstic acid (Fig. 1a). All the IR spectra of the catalysts showed characteristic skeletal vibrations of the Keggin structure, [$\nu(P-O)$ 1080–1085 cm^{-1} , $\nu(W=O)$ 977–987 cm^{-1} , $\nu(W-Ob-W)$ 895 cm^{-1} , $\nu(W-Oc-W)$ 813 cm^{-1}] [7,8,10], compared with 12-phosphotungstic acid (Fig. 2a). Our data suggest that the Keggin structure of the 12-phosphotungstic acid was still retained in the 12-phosphotungstate through the synthesis.

3.2. The catalytic oxidation of alcohols

The catalytic activities of these catalysts were compared during the solvent-free oxidation of octan-2-ol at 363 K and the results are given in Fig. 3. It can be seen from Fig. 3 that all these 12-phosphotungstate catalysts have catalytic activities for the oxidation of octan-2-ol. Catalysts **2a**, **3a**, and **4a**, which consisted of short-chain alkylammonium cations, showed low catalytic activities and a yield lower than 30%. The yield of 20% was obtained with catalyst **a**. These catalysts had a lower utilization efficiency of hydrogen peroxide, and most of the hydrogen peroxide was decomposed in the reaction. Therefore, we synthesized catalysts **1a**, **5a**,

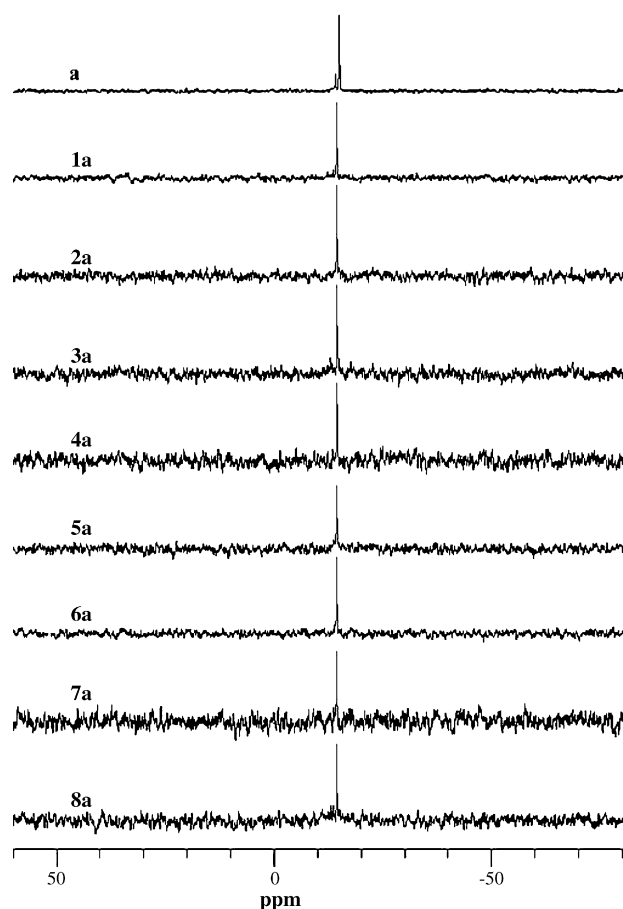


Fig. 1. The ^{31}P NMR spectra of catalysts **a** and **1a–8a** in DMF with a D_2O internal tube locking field. The catalyst **a** was in a mixture of DMF and H_2O ($v/v = 1:1$).

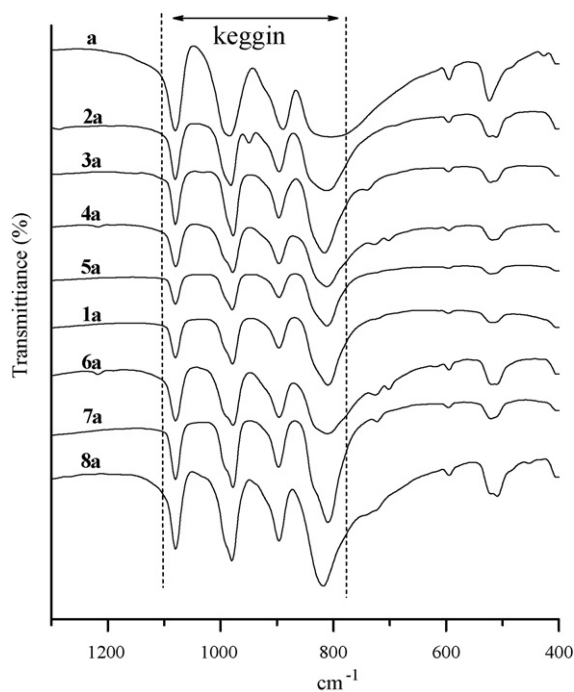
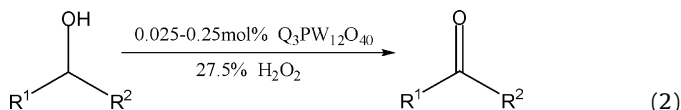


Fig. 2. The IR spectra of catalysts **a** and **1a–8a**.

6a, **7a**, and **8a** with long-chain alkylammonium cations which had the higher phase-transfer ability in the oil-water two-phase reaction. These catalysts showed high catalytic activity, and the yields of octan-2-one were above 80%. Among these catalysts, **1a** showed the highest catalytic activity, and the octan-2-one yield of 93% was obtained.



Based on the properties mentioned above, catalyst **1a** was employed to study oxidation of several secondary alcohols (Eq. (2)). As shown in Table 1, by following the procedure A, secondary alcohols were efficiently oxidized to the corresponding ketones under solvent-free conditions, and the yields of 86–95% were obtained. The results revealed that the catalyst **1a** had higher TON in the oxidation. The TON of catalyst **1a** was in the range of 344–380 (Table 1, Entries 3 and 15). Except for Ikegami's PW_{12} system [9], the TON of catalyst **1a** was higher than that of the PW_{12} and other similar catalytic systems reported before. Such as, in octan-2-ol oxidation, the TONs of Ishii's PW_{12} , Venturello's PW_4 , our early reported catalyst, Neumann's sandwich catalyst, and Wang's mono-substituted Keggin-polyoxometalate were 45 [6a], 192 [6b], 186 [6c], 227 [6d], and 356 [6g], respectively. Here, catalyst **1a** was as high as 372 (Table 1, Entry 7).

Although the TOF of **1a** was lower than that of Venturello's PW_4 system [6b] in octan-2-ol and 1-phenylethanol oxidations (Table 1, Entries 7 and 15), catalyst **1a** was recovered and reused easily in the oxidation recycle following the procedure A. The solid catalyst **1a** was dissolved in the organic phase during the reaction and precipitated from the system by adding petroleum ether to the mixture after the reaction. Then it was easily separated from the system, washed by diethyl ether, and dried for reuse. Octan-2-ol was oxidized by recovered **1a** with a slightly decreased yield (Table 1, Entries 8–10). The recovered **1a** still kept the original structure as monitored by ^{31}P MAS NMR and IR spectra (Fig. 4). In the oxidation of alcohols, the desired ketone was obtained in good yields when 0.25 mol% **1a** was used as catalyst and procedure A was followed. It should be noted that the excellent yield was also obtained by lengthening the reaction time to 12 h, even if the quantity of **1a** was decreased to 0.025 mol% in procedure B. Meanwhile, TON and TOF of **1a** were as high as 3840 and 320 h^{-1} , respectively (Table 1,

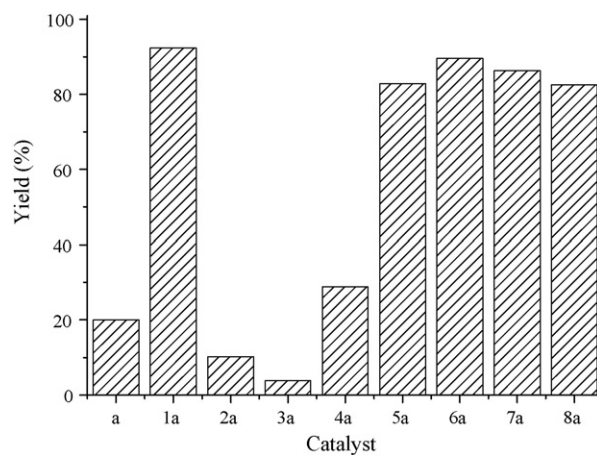


Fig. 3. Comparison of the catalytic activity in the octan-2-ol oxidation catalyzed by **a** and **1a–8a**. Reaction conditions: octan-2-ol (15 mmol), catalyst (25 μmol), hydrogen peroxide (27.5%, 10 mmol), 363 K, 6 h. The yields were determined by GC using an internal standard technique.

Table 1
The solvent-free oxidation of alcohols to ketones catalyzed by **1a**^a

Entry	Substrate	Procedure	Yield (%)	TON ^b	TOF ^c (h ⁻¹)
1	Pentan-2-ol	A	88	352	58
2 ^d	Pentan-2-ol	B	92	1840	153
3	4-Methylpentan-2-ol	A	86	344	57
4 ^d	4-Methylpentan-2-ol	B	94	1880	156
5	Cyclohexanol	A	90	360	60
6 ^e	Cyclohexanol	B	92	368	61
7	Octan-2-ol	A	93	372	62
8 ^f	Octan-2-ol	A	88	–	–
9 ^f	Octan-2-ol	A	86	–	–
10 ^f	Octan-2-ol	A	86	–	–
11	Octan-2-ol	B	96	3840	320
12 ^g	Octan-2-ol	C	45	–	–
13 ^h	Octan-2-ol	C	15	–	–
14 ⁱ	Octan-2-ol	C	90	–	–
15 ^j	1-Phenyethanol	A	95	380	126
16 ^k	1-Phenyethanol	B	95	3800	316

^a Reaction conditions: procedure A: alcohol (15 mmol), H₂O₂ (27.5%, 10 mmol) and **1a** (25 μmol), 363 K, 6 h, and the yield was determined by GC using an internal standard technique and based on hydrogen peroxide; procedure B: alcohol (500 mmol), H₂O₂ (27.5%, 750 mmol) and **1a** (125 μmol), 363 K, 12 h, and the isolated yield was obtained; procedure C: alcohol and H₂O₂ (27.5%) were all 10 mmol, **1a** (10 μmol), 363 K, 8 h.

^b The turnover number of the catalyst (mmol product/mmol Cat.).

^c The turnover frequency of the catalyst is TON per hour.

^d 250 μmol **1a**.

^e 10 mmol cyclohexanol, 15 mmol 27.5% H₂O₂ and 25 μmol **1a**, 6 h.

^f The experiment used the recycled **1a** [11] which was recovered by adding petroleum ether to the reaction system after the reaction, 1st reuse (Entry 8), 2nd reuse (Entry 9) and 3rd reuse (Entry 10).

^g The reaction time is 2 h.

^h The reaction was stopped after 2 h, the aqueous and organic phases were separated, and the 10 mmol fresh alcohol and 5 mmol H₂O₂ (27.5%) were added to the aqueous phase keeping on reaction for 8 h.

ⁱ The reaction was stopped after 2 h, the aqueous and organic phases were separated, and the 10 mmol fresh H₂O₂ (27.5%) was added to the organic phase keeping on reaction for 6 h.

^j 10 mmol 1-Phenyethanol, 3 h.

^k 10 mmol 1-Phenyethanol, 10 mmol 27.5% H₂O₂ and 2.5 μmol **1a**.

Entry 11). The TON and TOF of **1a** in 4-methylpentan-2-ol oxidation were also increased up to 1880 and 156 h⁻¹ in procedure B (Table 1, Entry 4). TON and TOF of catalyst **1a** remained in the oxidation of these alcohols when procedure B was followed.

3.3. The process of alcohol oxidation

It is well known that [PW₁₂O₄₀]³⁻ is degraded to PW₄ completely by excess hydrogen peroxide, which was able to be detected by ³¹P NMR (Fig. 5a), and that the PW₄ was the real active catalyst in alkene epoxidation [8a]. In our catalytic system, the real active catalyst was also the PW₄ species but not the PW₁₂ species. However, unlike the H₃PW₁₂O₄₀ catalyst, **1a** was not easily degraded to the PW₄ species in the presence of hydrogen peroxide. Even with over 400 equivalents hydrogen peroxide, the catalyst was only degraded partially, which was demonstrated from ³¹P NMR.

The catalyst electric conductivity was determined by dissolving catalyst **1a** (0.01 mmol) in 2 ml strongly polar DMF and in 2 ml weakly polar acetophenone. The electric conductivities of these two solutions were 654 and 85 μS/cm, which were different from 9 and 0.4 μS/cm for pure DMF and acetophenone. Thus, we concluded that the ionic compound **1a** was not ionized sufficiently in acetophenone. So the anion of catalyst **1a** did not form free ion entirely to react with hydrogen peroxide, and PW₄ was formed partially during treatment with hydrogen peroxide in acetophenone. But in strongly polar DMF, catalyst **1a** was almost fully ionized and able to be degraded to PW₄ species completely by reacting with

hydrogen peroxide. The ³¹P NMR spectra of **1a** reacting with hydrogen peroxide in DMF and acetophenone are shown in Fig. 5g and f, respectively. In the alcohol oxidation reaction, catalyst **1a** was not dissolved in the reaction system instantly at the beginning of the reaction, but it was dissolved while the reaction was progressing. The transformation of catalyst **1a** in the oxidation was the same as that in acetophenone when treated with hydrogen peroxide. It was suggested that the anion of **1a**, PW₁₂, was not a free anion in the alcohol oxidation, which only was ionized and degraded partially to PW₄, as detected by ³¹P NMR during the reaction (Fig. 5d).

The ³¹P NMR spectra of **1a** and **a** reacting with hydrogen peroxide are given in Fig. 5. The spectrum d showed that the PW₄ and PW₁₂ species coexisted in the organic phase during the reaction and in the aqueous phase only PW₄ was detected after 2 h (Fig. 5b). It was surprising that the active catalyst PW₄ disappeared and only the PW₁₂ existed in the organic phase after 8 h (Fig. 5e), while the PW₄ was still the only phosphor-tungsten species (Fig. 5c) in the aqueous phase. The ICP data showed that 42.6% of W and 17.5% of W were in the aqueous phase after 2 and 8 h, respectively (Table 2, Entries 2 and 3). After the reaction, the amount of W decreased in the aqueous phase and only the PW₁₂ species was left in the organic

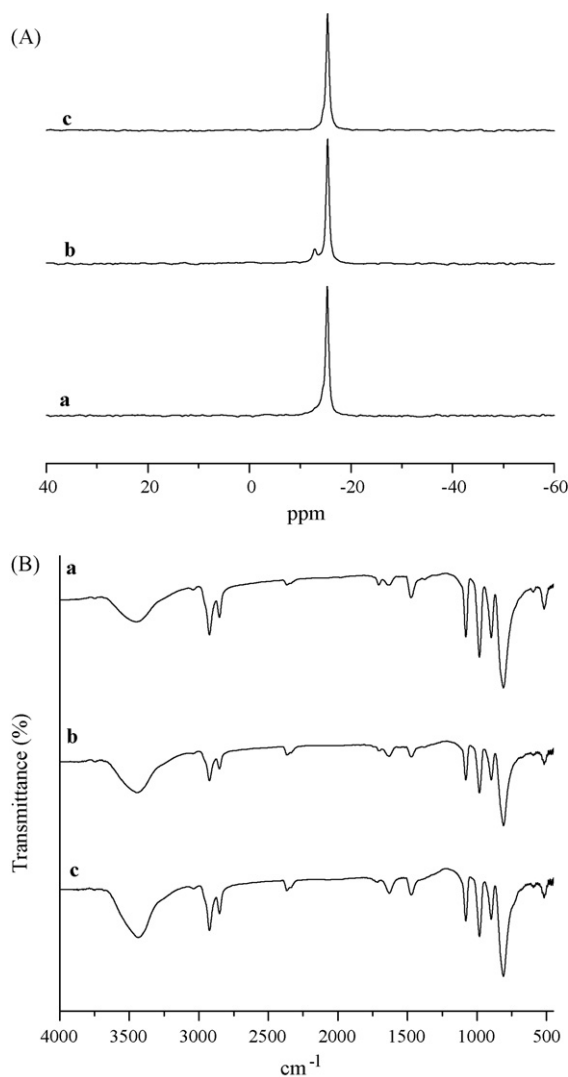


Fig. 4. The ³¹P MAS NMR and IR spectra of **1a** and recovered **1a**. Figures A and B are ³¹P MAS NMR and IR spectra of the catalyst **1a** and the recovered **1a**, respectively. (a) The fresh **1a**, (b) the recovered **1a** in the 1st cycle, (c) the recovered **1a** in the 3rd cycle.

oxidation, and the reaction mechanism was proposed as shown in Scheme 2.

4. Conclusion

In conclusion, $[n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_3\text{PW}_{12}\text{O}_{40}$ was employed to catalyze the oxidation of alcohols with 27.5% aqueous hydrogen peroxide under solvent-free conditions. The desired carbonyl compounds were obtained in satisfactory yields through procedure B with high TON and TOF. A novel transformation of species was discovered during alcohol oxidation with hydrogen peroxide catalyzed by $[n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_3\text{PW}_{12}\text{O}_{40}$. In the alcohol oxidation, the PW_{12} species was partially degraded to the PW_4 species by the reaction with hydrogen peroxide, which was the active species for catalyzing alcohol oxidation. Further more, it was the first time to report that the PW_4 and PW_{12} species were in equilibrium during the reaction, and most of the PW_4 species would be transformed to the PW_{12} species again after the reaction, which was quite different from the keystones of others in the alcohol oxidation catalyzed by 12-phosphotungstate.

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References

- [1] (a) M. Hudlicky, *Oxidations in Organic Chemistry*, ACS, Washington, DC, 1990; (b) R.A. Sheldon, I.C.W.E. Arends, A. Dijkstra, *Catal. Today* 57 (2000) 157–166.
- [2] (a) J.R. Holum, *J. Org. Chem.* 26 (1961) 4814–4816; (b) J.C. Collins, W.W. Hess, F.J. Frank, *Tetrahedron Lett.* 9 (1968) 3363–3366; (c) E.J. Corey, J.W. Suggs, *Tetrahedron Lett.* 16 (1975) 2647–2650; (d) R.J. Highet, W.C. Wildman, *J. Am. Soc. Chem.* 77 (1955) 4399–4401; (e) D.G. Lee, U.A. Spitzer, *J. Org. Chem.* 35 (1970) 3589–3590; (f) R.V. Stevens, K.T. Chapman, H.N. Weller, *J. Org. Chem.* 45 (1980) 2030–2032; (g) F.M. Menger, C. Lee, *J. Org. Chem.* 44 (1979) 3446–3448.
- [3] (a) B.M. Trost, *Science* 254 (1991) 1471–1477; (b) B.M. Trost, *Angew. Chem. Int. Ed.* 34 (1995) 259–281.
- [4] (a) G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636–1639; (b) P. Gamez, I.W.C.E. Arends, J. Reedijk, R.A. Sheldon, *Chem. Commun.* 19 (2003) 2414–2415; (c) N. Jiang, A.J. Ragauskas, *J. Org. Chem.* 76 (2006) 7087–7090; (d) N. Jiang, A.J. Ragauskas, *Tetrahedron Lett.* 48 (2007) 273–276; (e) A. Haimov, R. Neumann, *Chem. Commun.* 8 (2002) 876–877; (f) T.awahama, Y. Yoshino, T. Kertoku, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* 65 (2000) 6502–6507; (g) R.H. Liu, X.M. Liang, C.Y. Dong, X.Q. Hu, *J. Am. Chem. Soc.* 126 (2004) 4112–4113; (h) H.L. Wu, Q.H. Zhang, Y. Wang, *Adv. Synth. Catal.* 347 (2005) 1356–1360.
- [5] (a) P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 1998; (b) P.T. Anastas, L.B. Bartlett, M.M. Kirchoff, T.C. Williamson, *Catal. Today* 55 (2000) 11–22; (c) J.H. Clark, *Green Chem.* 1 (1999) 1–8; (d) R.A. Sheldon, *Green Chem.* 2 (2000) G1–G4.
- [6] (a) Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* 53 (1988) 3587–3593; (b) K. Yamawaki, H. Nishihara, T. Yoshida, T. Ura, H. Yamada, Y. Ishii, M. Ogawa, *Synth. Commun.* 18 (1988) 869–875; (c) Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, *J. Org. Chem.* 52 (1987) 1868–1870; (d) K. Yamawaki, T. Yoshida, H. Nishihara, Y. Ishii, M. Ogawa, *Synth. Commun.* 16 (1986) 537–541; (e) C. Venturello, M. Gambaro, *J. Org. Chem.* 56 (1991) 5924–5931; (f) S.J. Zhang, S. Gao, Z.W. Xi, J. Xu, *Catal. Commun.* 8 (2007) 531–534; (g) D. Sloboda-Rozner, P.L. Alsters, R. Neumann, *J. Am. Soc. Chem.* 125 (2003) 5280–5281; (h) B.S. Chhikara, R. Chandra, V. Tandon, *J. Catal.* 230 (2005) 436–439; (i) M. Carraro, L. Sandei, A. Sartorel, G. Scorrano, M. Bonchio, *Org. Lett.* 8 (2006) 3671–3674; (j) J. Wang, L. Yan, G. Li, X. Wang, Y. Ding, *J. Suo, Tetrahedron Lett.* 46 (2005) 7023–7027; (k) F.F. Bamoharram, M. Roshani, M.M. Heravi, S. Safaie, *Phosphorus Sulfur Silicon Relat. Elem.* 181 (2006) 2833–2841.
- [7] C. Venturello, R. D'Aloisio, *J. Org. Chem.* 53 (1988) 1553–1557.
- [8] (a) D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, *J. Am. Soc. Chem.* 117 (1995) 681–691; (b) C. Aubry, G. Chottard, N. Platzter, J.-M. Brégeault, R. Thowenot, F. Chauveau, C. Huet, H. Ledonl, *Inorg. Chem.* 30 (1991) 4409–4415; (c) L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Brégeault, *Inorg. Chem.* 33 (1994) 871–878.
- [9] H. Hamamoto, Y. Suzuki, Y.M.A. Yamada, H. Tabata, H. Takahashi, S. Ikegami, *Angew. Chem. Int. Ed.* 44 (2005) 4536–4538.
- [10] (a) L. Salles, J.Y. Piquemal, R. Thouvenot, C. Minot, J.M. Brégeault, *J. Mol. Catal. A Chem.* 117 (1997) 375–387; (b) N.M. Greckley, W.P. Griffith, A.C. Laemmel, H.S. Nogueira, B.C. Parkin, *J. Mol. Catal. A Chem.* 117 (1997) 185–198; (c) N.I. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fedotov, V.A. Likholobov, *J. Mol. Catal.* 114 (1996) 131–139; (d) L.R. Pizzio, C.V. Cáceres, M.N. Blanco, *Appl. Surf. Sci.* 151 (1999) 91–101; (e) E. Radkov, R.H. Beer, *Polyhedron* 14 (1995) 2139–2143.
- [11] The average catalyst recovery yield was 98 wt% during three recycles of octan-2-ol oxidation.