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# Selective aerobic oxidation of allyl phenyl ether to methyl ketone by palladium–polyoxometalate hybrid catalysts

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#### ABSTRACT

In this study, we report that selective aerobic oxidation of allyl phenyl ethers is attained by a Pd catalyst/polyoxometalate hybrid system to yield corresponding methyl ketones in water-enriched acetonitrile. The Pd  $(OAc)_2/H_5PV_2Mo_{10}O_{40}$  system exhibits higher conversions and yields of corresponding methyl ketone by Wacker-type oxidation of allyl phenyl ether as compared with the conventional PdCl<sub>2</sub>/CuCl<sub>2</sub> system. The higher yields are attributed to the efficient re-oxidation of Pd<sup>0</sup> to Pd<sup>2+</sup> by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> using O<sub>2</sub> as an oxidant as evidenced by electrochemical measurements. A reduced species of H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> by Pd<sup>0</sup> during the catalytic oxidation is revealed by UV-vis spectral measurements. The use of PdCl<sub>2</sub> in place of Pd(OAc)<sub>2</sub> in combination with  $[PV_2Mo_{10}O_{40}]^{5-}$  bearing tetraalkylammonium counter cations has also exhibited comparable conversions and product yields in the Wacker-type oxidation of allyl phenyl ethers. *Para*-substituted allyl phenyl ether derivatives are successfully oxidized in the Pd catalyst/polyoxometalate system to yield corresponding methyl ketones. The initial rate of products of *para*-substituted methyl ketones depended on the electronic effect of the substituents in which allyl phenyl ethers with electron-donating groups have accelerated the initial rate in the Pd catalyst/polyoxometalate system.

# 1. Introduction

Aerobic oxidation reactions play an important role in organic transformations. Selective aerobic oxidation of ethylene into acetaldehyde is known as the Wacker oxidation, in which PdCl<sub>2</sub> and CuCl<sub>2</sub> are used as a catalyst and a re-oxidation mediator of Pd<sup>0</sup>, respectively, in an HCl aqueous solution [1–7]. The PdCl<sub>2</sub>/CuCl<sub>2</sub> system has been applied for selective oxidation of terminal alkenes with long-chain alkyl, [8–10] aromatic [11], or cyclic [12] groups into corresponding ketones. However, the use of CuCl<sub>2</sub> yields undesired by-products of chlorides in long-chain olefins [13,14]. The corrosive condition of the PdCl<sub>2</sub>/CuCl<sub>2</sub> system can be a bottleneck for broad applications to other alkenes with functional groups.

In the Wacker-type oxidation reactions, allyl ethers bearing two reactive sites (allyl and ether groups) are regarded as difficult substrates because the oxygen atom in the vicinity of an allyl group can potentially coordinate to a Pd center, which can result in multiple side reactions such as hydrolysis that yield alcohols [15–17]. To avoid the hydrolysis of ether groups, some modifications have been developed for the Pd catalyst systems [18-20]. Alternative oxidants, solvents, and organic media were explored for the selective oxidation of allyl ethers [19, 21-24]. It should be a meaningful model to use allyl phenyl ethers, that are utilized as a raw material to gain versatile useful chemicals in electronic devices, as substrates for the Wacker-type oxidation [25]. For example, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (1.5 equiv) as an alternative oxidant was reported to oxidize allyl phenyl ether into corresponding ketone in good yield [23]. Similarly, Dess-Martin periodinane as an oxidant was also reported to oxidize allyl phenyl ether into corresponding methyl ketone [24]. In these reactions, oxidants generate large amounts of waste that are difficult to handle and remove from a product. As a consequence, it is required to develop environmentally benign catalytic systems for the Wacker-type oxidation of allyl ethers using molecular oxygen as an ideal oxidant.

Polyoxometalates (POMs) are promising candidates for catalytic

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oxidation reactions using molecular oxygen as an oxidant [26-31]. POMs are composed of molecular metal oxide anions that exhibit attractive features of redox properties [31]. In addition, the selection of counter cations of POMs, such as metal or organic cations, enables the control of their solubility to be used in a wide range of solvents [32]. Notably, the phosphovanadomolybdates,  $H_{3+x}PV_xMo_{12-x}O_{40}$  (x = 0–2), of the Keggin structure, which contains molybdenum and vanadium as addenda atoms, are reported to be efficient catalysts for aerobic oxidation and found to oxidize  $Pd^0$  to a  $Pd^{2+}$  species with molecular oxygen [28,33–35]. For example,  $PdSO_4/H_{3+x}PV_xMo_{12-x}O_{40}$  systems are used for the oxidation of but-1-ene to butan-2-one in the presence of O<sub>2</sub> [34]. Furthermore, the Pd(OAc)<sub>2</sub>/H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/tetrabutylammonium acetate system was reported to selectively oxidize alcohols to aldehydes using O<sub>2</sub> as an oxidant [35]. In this context, the combination of Pd catalysts and POMs as re-oxidation mediators is expected to be a potential system for the Wacker-type oxidation of allyl ethers into corresponding ketones. However, Wacker-type oxidation of allyl phenyl ethers has yet to be clarified in a Pd catalyst/POM system.

Herein, we report the Wacker-type oxidation of allyl phenyl ether derivatives by a catalytic system that uses Pd catalysts and  $\left[PV_2Mo_{10}O_{40}\right]^{5-}$  with various cations as re-oxidation mediators. The yields of the corresponding methyl ketones were achieved up to 74% in the Pd(OAc)/H<sub>5</sub>PV\_2Mo\_{10}O\_{40} system for the Wacker-type oxidation of allyl ethers using O<sub>2</sub> as an oxidant. The yields were significantly improved compared with the conventional PdCl<sub>2</sub>/CuCl<sub>2</sub> system. In this study, we have demonstrated that Pd catalyst/H<sub>5</sub>PV\_2Mo\_{10}O\_{40} can act as an efficient catalytic system for the Wacker-type oxidation of allyl phenyl ethers under mild conditions.

#### 2. Experimental

#### 2.1. General

Allyl phenyl ether, tetraethylammonium bromide, tetrabutylammonium bromide, tetrahexylammonium bromide, and tetradecylammonium bromide were purchased from Tokyo Chemical Industry Co., Ltd. Allyl 4-methoxy-, 4-fluoro-, 4-chloro-, and 4-bromophenyl ethers were synthesized according to literature procedure [36]. H<sub>3+x</sub>PV<sub>x</sub>Mo<sub>12-x</sub>O<sub>40</sub> (x = 0-2) were obtained commercially from Nippon Inorganic Colour & Chemical Co., Ltd. Tetraoctylammonium bromide and all palladium(II) reagents were purchased from Fujifilm Wako Pure Chemical Corp. All solvents for catalytic reactions were used without further purification. Gas chromatography was performed using Shimadzu GC-2014 equipped with an FID equipped with a TC-1 column (GL Science, 0.25 mm  $\times$  30 m).<sup>1</sup>H NMR spectral measurements were performed on a JEOL JNM-ECX 400 spectrometer using acetophenone as an internal standard. UV-vis spectral measurements at RT were performed using a SCINCO UV-vis spectrophotometer (S-3100). Electrochemical measurements were recorded on a potentiostat/galvanostat instrument (HZ-7000, HOKUTO DENKO). Purified water (18.2 MQ cm) was obtained from a Milli-Q system (Direct-Q3 UV, Millipore).

# 2.2. Synthesis of $TA_5PV_2Mo_{10}O_{40}$ (n = 2–10)

Protons of  $H_5PV_2Mo_{10}O_{40}$  were exchanged to tetraalkylammonium (TA) ions (n = 2–10) by a conventional method: Tetraalkylammonium bromide in methanol was slowly added to a methanol solution containing  $H_5PV_2Mo_{10}O_{40}$  and stirred at RT. The formed precipitate was filtered and recrystallized in acetonitrile/ethanol solution to give  $TA_5PV_2Mo_{10}O_{40}$ . The obtained samples were characterized by FT-IR to confirm the structure and presence of TA ions.

# 2.3. General procedure for Wacker-type oxidation of allyl phenyl ethers

A Pd catalyst (10 mol%) and a POM (3.0 mol%) re-oxidation mediator were added to the  $CH_3CN/H_2O$  (7:1, v/v) mixed solution containing allyl phenyl ether (0.10 M) at room temperature. The mixture was heated to target temperature and stirred for 16 h under ambient air. After the reaction, the mixture with biphenyl as an internal standard was quantified by GC-FID (Shimadzu, GC-2014). The temperature of the GC-FID program was kept 120 °C for 2 min, raised to 280 °C with a ramp rate of 10 °C/min and then kept for 2 min. The same procedure was used for <sup>1</sup>H NMR spectroscopic analysis but with the use of CD<sub>3</sub>CN/D<sub>2</sub>O (7:1, v/v) instead of CH<sub>3</sub>CN/H<sub>2</sub>O (7:1, v/v) as a reaction solution. Acetophenone was used as an internal standard for the quantification of products in the <sup>1</sup>H NMR spectroscopic analysis.

# 2.4. UV-vis spectroscopic analysis of reaction mixture

 $Pd(OAc)_2$  (10 mM),  $H_5PV_2Mo_{10}O_{40}$  (3.0 mM) were mixed in 4.0 mL of MeCN/H<sub>2</sub>O (7:1, v/v) mixed solution containing allyl phenyl ether (0.10 M) at RT under air. The reaction solution (100  $\mu$ L) was pretreated with a syringe filter (pore size: 0.20  $\mu$ m) to remove undissolved solid and then diluting in 2.9 mL of MeCN for UV–vis spectral measurements. UV–vis spectra of the solution were performed before reaction and after 2 h reaction at 60 °C. The control experiments for UV–vis spectroscopic analysis were conducted without the addition of Pd(OAc)\_2 or allyl phenyl ether in the reaction solution under the same procedure.

#### 2.5. Electrochemical measurements

Cyclic voltammograms of POMs (6.0–10 mM) and CuCl<sub>2</sub> (6.0 mM) were measured in MeCN under Ar atmosphere. All cyclic voltammograms were measured in three cycles. Electrolyte: 0.10 M TBAPF<sub>6</sub>, W.E.: Glassy carbon, C.E.: Pt wire, R.E.: Ag/AgNO<sub>3</sub>. Scan rate: 100 or 50 mV/s. Temperature: RT.

#### 3. Results and discussion

We used various Pd salts as Pd catalysts and POMs as re-oxidation mediators for the Wacker-type oxidation of allyl phenyl ether in a CH<sub>3</sub>CN/H<sub>2</sub>O (7:1, v/v) mixed solution at 60 °C under air atmosphere for 16 h. Products were quantified by gas chromatography with flame ionization detector (GC-FID) and also confirmed by <sup>1</sup>H NMR spectros-Three products, phenoxyacetone (methyl ketone), copy. phenoxypropan-1-al (aldehyde), and phenol were obtained from all the reactions (Table 1). Firstly, we have examined the effect of Pd catalysts in the Wacker-type oxidation reactions using  $H_5PV_2Mo_{10}O_{40}$  as a reoxidation mediator (Table1, entries 1-5). The use of PdCl<sub>2</sub> in the Wacker-type oxidation reaction showed good conversion (87%) and afforded methyl ketone and aldehyde in yield of 51% and 13%, respectively (Table 1, entry 1). This result is consistent with previous studies that methyl ketones formed by Wacker-type oxidation reactions are typically favored in accordance with Markovnikov's rule [5,37–40]. The highest conversion (100%) and methyl ketone yield (70%) were achieved by Pd(OAc)<sub>2</sub> (Table 1, entry 2). The use of Pd(NO<sub>3</sub>)<sub>2</sub> and Pd  $(OCOCF_3)_2$  has also exhibited high conversions as well as Pd $(OAc)_2$  in the Wacker-type oxidation reaction; however, the amount of phenol as the by-product was larger than that of Pd(OAc)<sub>2</sub> (Table 1, entries 3 and 4). No products were obtained by PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the Wacker-type oxidation (Table 1, entry 5). This can be ascribed to the strong coordination of the PPh<sub>3</sub> ligand to the Pd center preventing the coordination of the allyl moiety to Pd<sup>2+</sup>. Therefore, we demonstrate that a halogen-free catalytic system composed of Pd(OAc)<sub>2</sub> and H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> has exhibited selective oxidation of allyl phenyl ether into corresponding methyl ketone using O2 as an oxidant. Additionally, when the re-oxidation mediator of  $H_5PV_2Mo_{10}O_{40}$  was replaced to  $H_4PVMo_{11}O_{40}$  and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (Table 1, entries 6 and 7), the conversions and methyl ketone yields gradually decreased in the Wacker-type oxidation reactions. The decrease of the conversions and methyl ketone yields may be reflected in the reduction potentials of the POMs that H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> has a lowest oxidation power ( $E_{1/2} = +0.20$  V vs Ag/AgNO<sub>3</sub>) among

#### Table 1

Conversions and products yield obtained in Wacker-type oxidation of allyl phenyl ether.

$ \underbrace{\prod_{\text{Entry}}^{O}}_{\text{Entry}} \underbrace{\begin{array}{c} 10 \text{ mol}\% \text{ Pd catalyst} \\ \text{Re-oxidadtion mediator} \\ \text{CH}_3\text{CN/H}_2\text{O} (7:1, \text{v/v}) \\ \text{60 °C, 16 h} \end{array}}_{\text{CH}_3\text{CN/H}_2\text{O} (7:1, \text{v/v})} \underbrace{\begin{array}{c} 0 \\ \text{CH}_3\text{CN/H}_2\text{O} \end{array}}_{\text{CN/H}_2\text{O} (7:1, \text{v/v})} \underbrace{\begin{array}{c} 0 \\ \text{CH}_3\text{CN/H}_2\text{O} (7:1, \text{v/v})} \underbrace{\begin{array}{c} 0 \\ \text{CH}_3\text{CN/H}_2\text{O} \end{array}}_{\text{CN/H}_2\text{O} (7:1, \text{v/v})} \underbrace{\begin{array}{c} 0 \\ \text{CH}_3\text{CN/H}_2\text{O} (7:1, \text{v/v})} \underbrace{\begin{array}{c} 0 \\ \text{CN/H}_2\text{CN/H}_2\text{O} (7:1, \text{v/v})} \underbrace{\begin{array}{c} 0 \\ CN$											
	Pd catalyst	Re-oxidation mediator	Conv. (%)	Methyl Ketone Yield (%)	Aldehyde Yield (%)	Phenol Yield (%)					
1	PdCl <sub>2</sub>	H5PV2M010O40	87	51	13	13					
2	Pd(OAc) <sub>2</sub>	H <sub>5</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub>	100	70	14	9					
3	Pd(NO <sub>3</sub> ) <sub>2</sub>	H <sub>5</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub>	99	58	9	24					
4	Pd(OCOCF <sub>3</sub> ) <sub>2</sub>	H <sub>5</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub>	98	52	11	27					
5	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	H5PV2M010O40	2	0	0	0					
6	Pd(OAc) <sub>2</sub>	H <sub>4</sub> PVMo <sub>11</sub> O <sub>40</sub>	100	65	12	14					
7	Pd(OAc) <sub>2</sub>	$H_{3}PMo_{12}O_{40}$	41	23	6	6					
8	PdCl <sub>2</sub>	CuCl <sub>2</sub>	35	19	7	5					
9 <sup>a</sup>	PdCl <sub>2</sub>	CuCl <sub>2</sub>	28	16	7	4					
10 <sup>b</sup>	PdCl <sub>2</sub>	$H_5PV_2Mo_{10}O_{40}$	34	18	6	7					

Solvent: CH<sub>3</sub>CN/H<sub>2</sub>O (7:1, v/v), reaction time: 16 h, reaction temperature: 60 °C, [Allyl phenyl ether]: 100 mM, [Pd catalyst]: 10 mM, [Re-oxidation mediator]: 3.0 mM. Products were quantified by GC-FID.

<sup>a</sup> [CuCl<sub>2</sub>]: 10 mM.

<sup>b</sup> Under Ar.

those POMs (Fig. S1 in the Supplementary materials).

In comparison with the higher conversion and methyl ketone yield by the combination of PdCl<sub>2</sub> and H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>, the use of PdCl<sub>2</sub> and CuCl<sub>2</sub>, the conventional Wacker catalysts, results in a low conversion (34%) with 19% of methyl ketone yield in the Wacker-type oxidation reactions (Table 1, entry 8). The result demonstrates that the conversion and product yields are significantly improved by the use of  $H_5PV_2Mo_{10}O_{40}$  in the Wacker-type oxidation reactions. Additionally, the increase of CuCl<sub>2</sub> concentrations has suppressed the conversion to 28% (Table 1, entry 9), suggesting that CuCl<sub>2</sub> may disturb the coordination of the allyl moiety to Pd<sup>2+</sup>. This also indicates the advantage of  $H_5PV_2Mo_{10}O_{40}$  as a re-oxidation mediator for the oxidation of Pd<sup>0</sup> to  $Pd^{2+}$ . The enhancement of the re-oxidation process can be explained by the difference in reduction potentials between H5PV2M010O40 and CuCl<sub>2</sub>. The reduction potential of  $H_5PV_2Mo_{10}O_{40}$  ( $E_{1/2} = +0.43$  V vs Ag/ AgNO<sub>3</sub>) is higher than that of CuCl<sub>2</sub> ( $E_{1/2} = +0.18$  V vs Ag/AgNO<sub>3</sub>), which is determined by electrochemical measurements in MeCN (Fig. S2). A blank test was also examined by the combination of PdCl<sub>2</sub> and H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> in the absence of O<sub>2</sub>. The conversion was dramatically suppressed to 34% under argon atmosphere (Table 1, entry 10), indicating that O<sub>2</sub> was indispensable for the Wacker-type oxidation reactions.

To gain insight into the catalytic cycle of the Wacker-type oxidation of allyl phenyl ether, the effects of reaction temperature on the conversions and product yields were investigated using the Pd(OAc)<sub>2</sub>/ H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> system as shown in Fig. 1. The results revealed that high conversions of allyl phenyl ether were attained within the range of 30-70 °C. The highest yield for methyl ketone was obtained to be 74% when the reaction was performed at 30 °C. The yields of methyl ketone and aldehyde decreased with increase in temperature, whereas the phenol yield increased. This result agrees with the fact that hydrolysis of ether moieties is generally facilitated with execution at high temperature [41]. When the reaction was performed at 80 °C, black precipitates derived from Pd<sup>0</sup> nanoparticles were observed in the solutions, resulting in a low conversion (41%). Thus, the results indicate that the Wacker-type oxidation of allyl phenyl ether by the Pd(OAc)<sub>2</sub>/H<sub>5</sub>PV<sub>2</sub>-Mo10Q40 system is accelerated at low temperatures and competed with phenol production derived from the hydrolysis of ether moieties at high temperatures.

We have also measured the UV–vis spectral changes to monitor intermediates formed during the Wacker-type oxidation reactions in the catalytic system of Pd(OAc)<sub>2</sub>/H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (Fig. 2). The reaction solution containing Pd(OAc)<sub>2</sub>, H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>, and allyl phenyl ether exhibited a characteristic absorption band around 720 nm at initial



Fig. 1. Temperature dependence of conversions and product yields in the Wacker-type oxidation of allyl phenyl ether. Solvent:  $CH_3CN/H_2O$  (7:1, v/v), reaction time: 16 h, [Allyl phenyl ether]: 100 mM,  $[Pd(OAc)_2]$ : 10 mM,  $[H_5PV_2Mo_{10}O_{40}]$ : 3.0 mM.

reaction time and after 2 h at 60 °C (Fig. 2a), which was not observed on the reaction solution in the absence of the Pd catalyst or allyl phenyl ether. This suggests that the characteristic absorption band around 720 nm is derived from the reduced species of  $H_5PV_2Mo_{10}O_{40}$ . The characteristic absorption band was also observed in a separate experiment in which hydroquinone, a reductant, was added into  $H_5PV_2Mo_{10}O_{40}$  in MeCN (Fig. 2b), indicating the formation of  $[PV^VV^{IV}Mo_{10}O_{40}]^{6-}$ (POM<sub>red</sub>). Thus, these results clearly indicate that the formed species in the reaction solution is attributed to POM<sub>red</sub>. As POM<sub>red</sub> is observed in the catalytic reactions, the rate-determining step could be involved in the oxidation of POM<sub>red</sub> by molecular oxygen in the Pd(OAc)<sub>2</sub>/  $H_5PV_2Mo_{10}O_{40}$  system for the Wacker-type oxidation reactions.

According to previously reported literature, [6,42] the catalytic cycle in the Wacker-type oxidation of allyl phenyl ether using the Pd/POMs system is displayed in Scheme 1. The Wacker-type oxidation of allyl



**Fig. 2.** (a) UV–vis spectra of reaction solution containing  $H_5PV_2Mo_{10}O_{40}$  (3.0 mM), Pd(OAc)<sub>2</sub> (10 mM), and allyl phenyl ether (0.10 M) for reaction time of 0 and 2 h at 60 °C, and the solutions in the absence of Pd(OAc)<sub>2</sub> or allyl phenyl ether. (b) UV–vis spectral changes in POM<sub>ox</sub> (0.50 mM) with addition of 1.5 mM of hydroquinone as reductant to form POM<sub>red</sub> in MeCN. Inset: The absorption changes monitored at 765 nm against the hydroquinone concentrations.

phenyl ether by  $Pd^{2+}$  results in the formation of  $Pd^0$  that is then oxidized by  $[PV_2^VMo_{10}O_{40}]^{5-}$  (POM<sub>ox</sub>) to regenerate  $Pd^{2+}$ . The Reduced POM, which is assigned to  $[PV^VV^{IV}Mo_{10}O_{40}]^{6-}$  (POM<sub>red</sub>) by the cyclic voltammograms in Fig. S1, reacts with O<sub>2</sub> to produce POM<sub>ox</sub>. Based on the results in Table 1 and UV–vis spectra in Fig. 2, the use of  $H_5PV_2Mo_{10}O_{40}$  of can prevent from the formation of Pd nanoparticles, resulting in the high conversions and methyl ketone yields in the Wacker-type oxidation of allyl phenyl ether.

We have also investigated the influence of the counter cations of POM on the Wacker-type oxidation of allyl phenyl ether because the cation-POM interaction is known to be crucial to control their properties [19]. We have employed tetraalkylammonium (TA) cations with different alkyl chain lengths (n) as counter cations of  $[PV_2Mo_{10}O_{40}]^{5-}$  to examine the effect of the counter cations.  $TA_5PV_2Mo_{10}O_{40}$  (n = 2–10) were prepared by a typical method of cation exchange and characterized by Fourier transform infrared (FT-IR) spectra (Fig. S3). Unexpectedly,  $Pd(OAc)_2/TA_5PV_2Mo_{10}O_{40}$  (n = 6) exhibited low conversions in the Wacker-type oxidation of allyl phenyl ether (Table 2, entry 1). After the reaction, a black precipitate was observed in the solution, indicating insufficient re-oxidation of Pd<sup>0</sup> to Pd<sup>2+</sup> in the combination of Pd(OAc)<sub>2</sub> and  $TA_5PV_2Mo_{10}O_{40}$  (n = 6). On the other hand, the PdCl<sub>2</sub>/TA<sub>5</sub>PV<sub>2</sub>.  $Mo_{10}O_{40}$  (n = 6) system showed a relatively high conversion (93%) and afforded methyl ketone (56%) and aldehyde (15%) with a higher yield (Table 2, entry 2) compared with that of obtained from the PdCl<sub>2</sub>/H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> system (Table 1, entry 1). In the case of  $PdCl_2/TA_5PV_2Mo_{10}O_{40}$  (n = 6) system, no black precipitate was observed after the reaction, suggesting efficient re-oxidation of Pd<sup>0</sup> to  $Pd^{2+}$ . Furthermore, the temperature dependence of yield and conversion in the use of  $PdCl_2/TA_5PV_2Mo_{10}O_{40}$  (n = 6) was also investigated during the Wacker-type oxidation of allyl phenyl ether, and the highest conversions and yields were obtained at 60 °C (Fig. S4). Meanwhile, it was found that the alkyl chain lengths (n) of TA cations has less affected the conversions and product yields in the  $PdCl_2/TA_5PV_2Mo_{10}O_{40}$  (n = 2–10) (Table 2, entries 3–7). Thus, these results demonstrate that the combination of Pd sources with POMs bearing alternative counter cations is critical for the Wacker-type oxidation of allyl phenyl ether.

Substituent effects of allyl phenyl ether were investigated for the Wacker-type oxidation in the  $PdCl_2/TA_5PV_2Mo_{10}O_{40}$  (n = 6) system (Fig. 3a). The corresponding methyl ketones quantified by<sup>1</sup>H NMR yielded in the reactions using para-substituted allyl phenyl ether derivatives (X = H, OMe, F and Cl) as substrates (Fig. S5). Fig. 3b shows the time courses of the corresponding methyl ketones obtained in the reactions. The initial rates for the production of methyl ketones were calculated from the slopes and determined to be  $3.74\times 10^{-5}\,M\,\text{min}^{-1}$  for H, 4.53  $\times$  10  $^{-5}$  M min  $^{-1}$  for OMe, 2.54  $\times$  10  $^{-5}$  M min  $^{-1}$  for F and 2.46  $\times$ 10<sup>-5</sup> M min<sup>-1</sup> for **Cl**. An allyl phenyl ether derivative having an electrondonating group (OMe) exhibited the highest initial rates as compared with those having electron-withdrawing groups (F and Cl). The initial rates of the Wacker-type oxidations were dependent on the Hammett parameters [43] of the substituents of the allyl phenyl ethers (Fig. 3c). The Hammett plots obtained for the para-substituted allyl phenyl ether derivatives showed a negative slope ( $\rho = -1.18$ ) as shown in Fig. 3c. The results demonstrate that the initial rates lineally depend on the  $\sigma_n$  value of the substituents. Thus, the use of allyl phenyl ether derivatives having



Scheme 1. Catalytic cycle in Wacker-type oxidation of allyl phenyl ether derivatives by Pd catalyst/POM hybrid system in this study.

Table 2

Dependence of alkyl chain length of counter cations to POM in the Wacker-type oxidation of allyl phenyl ether.

Entry	Pd catalyst	Re-oxidation mediator	Conv. (%)	Methyl Ketone Yield (%)	Aldehyde Yield (%)	Phenol Yield (%)
1 <sup>a</sup>	Pd(OAc) <sub>2</sub>	$TA_5PV_2Mo_{10}O_{40} n = 6$	66	33	13	15
$2^{a}$	PdCl <sub>2</sub>	$TA_5PV_2Mo_{10}O_{40} n = 6$	93	56	15	17
3	PdCl <sub>2</sub>	$TA_5PV_2Mo_{10}O_{40} n = 2$	97	60	21	10
4	PdCl <sub>2</sub>	$TA_5PV_2Mo_{10}O_{40} n = 4$	90	53	22	10
5	PdCl <sub>2</sub>	$TA_5PV_2Mo_{10}O_{40} n = 6$	98	58	19	12
6	PdCl <sub>2</sub>	$TA_5PV_2Mo_{10}O_{40} n = 8$	97	60	23	11
7	PdCl <sub>2</sub>	$TA_5 PV_2 Mo_{10}O_{40} \; n = 10$	99	61	23	11

Solvent: CH<sub>3</sub>CN/H<sub>2</sub>O (7:1, v/v), reaction time: 16 h, reaction temperature: 60 °C, [Allyl phenyl ether]: 100 mM, [Pd catalyst]: 10 mM, [Re-oxidation mediator]: 3.0 mM. Products were quantified by GC-FID.

<sup>a</sup> At 70 °C.



**Fig. 3.** (a) Schematic representation of the Wacker-type oxidation of *para*-substituted allyl phenyl ether derivatives (X = H, **OMe**, F and **Cl**) in the PdCl<sub>2</sub>/TA<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (n = 6) system. (b) Time courses of the corresponding methyl ketones quantified by <sup>1</sup>H NMR in the reaction solutions (CD<sub>3</sub>CN/D<sub>2</sub>O (7:1, v/v)) containing TA<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (n = 6) (1.5 mM), PdCl<sub>2</sub> (5.0 mM), and *para*-substituted allyl phenyl ether derivatives (0.10 M) at 25 °C. (c) Hammett plots for the Wacker-type oxidation of *para*-substituted allyl phenyl ether derivatives.

electron-donating groups can accelerate the Wacker-type oxidation in the  $PdCl_2/TA_5PV_2Mo_{10}O_{40}$  (n = 6) system.

#### 4. Conclusions

In summary, we have found that the Pd(OAc)<sub>2</sub>/H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> system successfully catalyzed the Wacker-type oxidation of allyl phenyl ether, which is regarded as a difficult substrate that has two reactive sites, into corresponding methyl ketone in good yield (74%) using molecular oxygen as an ideal oxidant at low temperature (30 °C). The yield of methyl ketone obtained in the Pd(OAc)<sub>2</sub>/H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> system is higher than that in the conventional PdCl<sub>2</sub>/CuCl<sub>2</sub> system for the Wackertype oxidation of allyl phenyl ether. The electrochemical measurements of H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> and CuCl<sub>2</sub> in MeCN revealed that efficient reoxidation of Pd<sup>0</sup> to Pd<sup>2+</sup> by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> resulted in a high conversion and a yield for the Wacker-type oxidation. A reduced species of H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> observed during the catalytic reaction was confirmed by UV-vis spectral measurements. Para-substituted allyl phenyl ether derivatives are also oxidized to yield corresponding methyl ketones in the  $PdCl_2/TA_5PV_2Mo_{10}O_{40}$  (n = 6) system. The Hammett plots indicate a substituent effect that substrates with electron-donating groups have enhanced the initial rates for Wacker-type oxidation of allyl phenyl ether derivatives. Finally, the use of  $\left[PV_2Mo_{10}O_{40}\right]^{5-}$  bearing appropriate counter anions as re-oxidation mediators and Pd catalysts are key features in the selective oxidation of allyl phenyl ethers under mild conditions. Thus, we expect that the combination of Pd catalysts with POMs can be applied to various selective oxidation reactions using O2 as a green oxidant in synthetic and catalytic chemistry.

#### CRediT authorship contribution statement

Satoru Tamura: Data curation, Writing - original draft. Yoshihiro Shimoyama: Data curation, Writing - review & editing, Funding acquisition. Dachao Hong: Conceptualization, Writing - review & editing, Funding acquisition, Supervision. Yoshihiro Kon: Conceptualization, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111178.

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