ตัวเร่งปฏิกิริยาพอลิออกโซเมทาเลตที่แทนที่ด้วยเวเนเดียม สำหรับออกซิเดชันของไซโคลแอลเคนและแอลกอฮอล์ ด้วยไฮโดรเจนเปอร์ออกไซด์

VANADIUM (V)-SUBSTITUTED POLYOXOMETALATE CATALYST FOR OXIDATION OF CYCLOALKANES AND ALCOHOLS WITH HYDROGEN PEROXIDE

วิมลรัตน์ ตระการพฤกษ์
Wimonrat Trakarnpruk

ภาควิชาเคมี คณะวิทยาศาสตร์ และศูนย์ความเป็นเลิศด้านปิโตรเลียม ปิโตรเคมีและวัสดุขั้นสูง
จุฬาลงกรณ์มหาวิทยาลัย
Department of Chemistry, Faculty of Science, and Center of Excellence for Petroleum,
Petrochemicals, and Advanced Materials, Chulalongkorn University, Thailand.

***Corresponding author, E-mail**: wimonrat.t@chula.th*

บทคัดย่อ

        งานวิจัยนี้ได้สังเคราะห์และทำการพิสูจน์เอกลักษณ์ของเกลือเททราบิวทิลแอมโมเนียม ของพอลิออกโซเมทาเลตชนิดเคกกิง แสดงผลของออกซิเดชันของไซโคลแอลเคนและแอลกอฮอล์ด้วย ตัวเร่งปฏิกิริยาพอลิออกโซเมทาเลตที่ถูกแทนที่ด้วยวาเนเดียม$[(n\text{-}C_9H_9)_4N)]_4[PW_{11}VO_{40}]$และไม่ได้ถูกแทนที่ $[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$ โดยใช้ไฮโดรเจนเปอร์ออกไซด์เป็นสารออกซิไดซ์ สำหรับออกซิเดชันที่เร่งปฏิกิริยา ระบบเอกพันธ์ของไซโคลเฮกเซน และไซโคลออกเทน พบว่าตัวเร่งปฏิกิริยาชนิดที่ถูกแทนที่ด้วยวาเนเดียม มีประสิทธิภาพสูงกว่าภายใต้ภาวะปฏิกิริยาเดียวกัน ทั้งนี้เนื่องจากความสามารถในการรีดิวซ์ของวาเนเดียม ตัวเร่งปฏิกิริยาทั้งสองชนิดให้ความเลือกจำเพาะต่อคีโทนสูงกว่าแอลกอฮอล์และเกิดไซโคลแอลคิลไฮโดรเปอร์ ออกไซด์ขึ้นด้วย ภายใต้ภาวะปฏิกิริยา: สารตั้งต้น 23 มิลลิโมล ตัวเร่งปฏิกิริยา 0.05 มิลลิโมล สัดส่วน โดยโมล H_2O_2/สารตั้งต้น = 3 CH_3CN 5 มิลลิลิตร อุณหภูมิของปฏิกิริยา 70 องศาเซลเซียส เวลา 8 ชั่วโมง ตัวเร่งปฏิกิริยา$[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$ ให้ผลการเปลี่ยนรูปของไซโคลเฮกเซน และไซโคลออกเทน 63% และ 70% โดยมีความเลือกจำเพาะต่อคีโทน 52% และ 50% ตามลำดับ สำหรับออกซิเดชันของแอลกอฮอล์ ด้วยตัวเร่งปฏิกิริยา $[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$ ได้ทำปฏิกิริยาโดยไม่มีตัวทำละลายใดๆ เติมลงไป เป็นระบบสองวัฏภาค (น้ำ–แอลกอฮอล์) พบว่าไซโคลเฮกซานอลถูกออกซิไดซ์เป็นไซโคลเฮกซาโนน โดยมีค่าการเปลี่ยนรูป 92% ความเลือกจำเพาะ 100% ในขณะที่เบนซิลแอลกอฮอล์ถูกออกซิไดซ์เป็น เบนซัลดีไฮด์ โดยมีค่าการเปลี่ยนรูป 88% ความเลือกจำเพาะ 100% ภายใต้ภาวะปฏิกิริยา: สารตั้งต้น

23 มิลลิโมล ตัวเร่งปฏิกิริยา 0.05 มิลลิโมล สัดส่วนโดยโมล H_2O_2/สารตั้งต้น = 2 อุณหภูมิของปฏิกิริยา 90 องศาเซลเซียส เวลา 3 ชั่วโมง กลไกของปฏิกิริยาเกิดผ่านแรดิเคิล สามารถนำตัวเร่งปฏิกิริยามาใช้ซ้ำได้ 3 ครั้งโดยมีประสิทธิภาพลดลงเพียงเล็กน้อย

คำสำคัญ: พอลิออกโซเมทาเลต วาเนเดียม ออกซิเดชัน แอลกอฮอล์ ไซโคลแอลเคน ไฮโดรเจนเปอร์ออกไซด์

Abstract

In this research the tetrabutylammonium salts of the Keggin-type polyoxometalates were synthesized and characterized. The results on oxidation of cycloalkanes and alcohols over vanadium(V)-substituted polyoxometalate catalyst, $[(n-C_4H_9)_4N)]_4[PW_{11}VO_{40}]$ and unsubstituted polyoxometalate catalyst, $[(n-C_4H_9)_4N]_3[PW_{12}O_{40}]$ with hydrogen peroxide as an oxidant are presented. For the homogeneously catalyzed oxidation of cyclohexane and cyclooctane, the vanadium(V)-substituted catalyst is found to be more active under the same reaction condition. This is due to reducibility of vanadium. Both catalysts gave higher selectivity to ketone than alcohol. Cycloalkyl hydroperoxide was also formed. Under reaction conditions of: substrate 23 mmol, catalyst 0.05 mmol, H_2O_2/substrate molar ratio = 3, CH_3CN 5 ml, reaction temperature 70°C, time 8 h, the $[(n-C_4H_9)_4N]_4[PW_{11}VO_{40}]$ yielded 63% and 70% conversion with 52% and 50% selectivity to ketone, respectively for oxidation of cyclohexane and cyclooctane. For the oxidation of alcohols, the reactions were performed over the $[(n-C_4H_9)_4N]_4[PW_{11}VO_{40}]$ in the absence of any added solvent, as a two-phase system (aqueous-alcohol). Cyclohexanol was oxidized to cyclohexanone with 92% conversion and 100% selectivity whereas benzyl alcohol was oxidized to benzaldehyde with 88% conversion and 100% selectivity under the reaction conditions of: substrate 23 mmol, catalyst 0.05 mmol, H_2O_2/substrate molar ratio = 2, reaction temperature 90°C and time 3 h. Reaction mechanism is shown to occur via radical pathway. The catalysts can be reused 3 times with slight decrease in activity.

Keywords: Polyoxometalate, Vanadium, Oxidation, Alcohols, Cycloalkanes, Hydrogen peroxide

Introduction

The selective oxidation of organic substrates is an important transformation in organic synthesis. The oxidation of alcohols to aldehydes or ketones is a fundamental preparative reaction, which has been widely investigated using various catalytic systems and hydrogen peroxide as oxidant. However, some organic substrates are insoluble in aqueous hydrogen peroxide, which can subsequently lower the selectivity and efficiency of the oxidation reaction. The use of a phase transfer catalyst (PTC) was reported [1].

Selective oxidation of cyclohexane to cyclohexanol and cyclohexanone is an important reaction since cyclohexanol and cyclohexanone are the key intermediates in the production of adipic acid (Nylon-66) and caprolactam (Nylon-6). Homogeneous catalysis using soluble transition metal salts (such as cobalt naphthenate) is the only technology actually developed until now. In this process, the oxidation is carried out at 150°C and 1-2 MPa air pressure. This affords ca. 4% conversion and 70-85% selectivity to cyclohexanone and cyclohexanol. The conversion is limited to less than 10% to avoid over-oxidation to unwanted products, since the primary products: cyclohexanone and cyclohexanol are more reactive than cyclohexane [2]. Cyclohexane oxidation under mild reaction conditions has been successfully carried out with many transition metal substituted polyoxometalates using either H_2O_2 or tert-butyl hydroperoxide (TBHP) as oxygen donors [3-5].

The oxidation of alcohols to aldehydes or ketones is a vital reaction in synthetic organic chemistry. Homogeneous catalysts [6] and heterogeneous catalysts have been reported including several heteropoly oxometalates using H_2O_2 [7] or oxygen as oxidant [8-9]

Polyoxometalates, In particular, Keggin-type, $[PM_{12}O_{40}]^{n-}$ (M = Mo or W) (Figure 1) consist of a central PO_4 tetrahedron, surrounded by 12 MO_6 octahedra arranged in four groups of three edge sharing M_3O_{13}. Each group shares a common oxygen atom, together with the central PO_4 tetrahedron. Polyoxometalates are unique catalytic materials, due to their multifunctionality and structural mobility. Their acid and redox properties can be tuned by varying polyanion composition. Their activities can be controlled by changes in the metal center and the counter cation. Metal substituted heteropolyoxometalates do similarly to metal complexes of macrocyclic ligands, metalloporphyrins and related species, because they posses rigid co-ordination sites surrounding a metal centre [10]. The robust nature of the polyoxometalate ligands and their resistance to oxidation, the possibility of working with these species in both polar and nonpolar solvents lead to valuable applications in catalysis. Polyoxometalates catalyzed oxidation reactions with H_2O_2 have been studied, such as $[n-C_7H_7N(CH_3)_3]_7PW_{11}O_{39}$ ([11], $[n-C_{16}H_{33}N(CH_3)_3]_3 PW_{12}O_{40}$ [12] and $H_5PV_2Mo_{10}O_{40}$ [13]. It is possible to substitute Mo^{6+} or W^{6+} ions by V^{5+}, thus creating an excess of negative charge which has to be compensated [14]. The vanadium-substituted heteropolymetalates were shown to be effective catalysts for many oxidation reactions. [15-16] including oxidative desulfurization reported in our previous work [17]. It was reported that vanadium polyoxometalate $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}]_3.H_2O$ catalyzed oxidation of benzylic alcohols in presence of p-toluenesulphonic acid (PTSA) but not cyclohexanol [18].
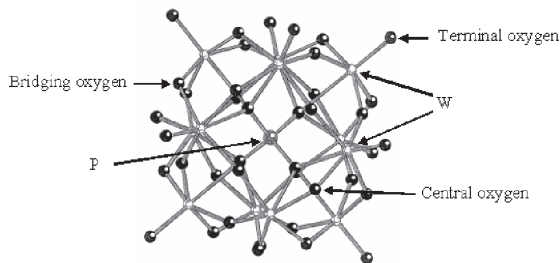
Figure 1. Structure of Keggin polyoxometalate.

Objectives

1. To synthesize and characterize vanadium(V)-substituted and unsubstituted polyoxometalates catalysts, $[(n\text{-}C_4H_9)_4N]_4$ $[PW_{11}VO_{40}]$ and $[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$

2. To study the oxidation of cycloalkanes and alcohols with H_2O_2 as an oxidant. Hydrogen peroxide was chosen as an oxidant since it is inexpensive, easily available, easy to handle and gives only water and oxygen as the products of decomposition.

Methods

Materials

Analytical grade of $Na_2WO_4 2H_2O$, $NaH_2PO_4 2H_2O$, NH_4VO_3, $(n\text{-}C_4H_9)_4NBr$, sulfuric acid concentrate, hydrochloric acid concentrate, diethyl ether, cyclohexane, cyclooctane, cyclohexanol, benzyl alcohol, $85\%H_3PO_4$, aqueous $30\%H_2O_2$, acetonitrile were obtained from either Fluka Chemie or Merck.

Analytical Methods

FT-IR spectra of the catalysts were recorded on a Nicolet FT-IR Impact 410 Spectrophotometer as KBr discs. Elemental analysis was performed using Inductive Coupled Plasma emission (ICP, Perkin Elmer model PLASMA-1000). UV-vis was recorded using 2550 spectrophotometer Shimadzu UV probe. Products from the oxidation reaction were analyzed by Gas Chromatograph, GC (a Varian CP-3800, equipped with a CP-Wax column (30 m. x 0.32 mm.) and FID as detector).

Syntheses of Catalysts

Part I. Preparation of $[(n\text{-}C_4H_9)_4N]_3$ $[PW_{12}O_{40}]$

0.5 g of $Na_2WO_4 2H_2O$ was dissolved in 5 mL water, 0.2 mL of $85\%H_3PO_4$ and 0.5 mL of concentrated sulfuric acid were then added, and the resulting suspension was stirred at room temperature for 12 h. Addition of 3 mL of water yielded a clear solution to which 0.14 g of $(n\text{-}C_4H_9)_4NBr$ was added immediately. After 15 min of stirring, the precipitate was filtered, then washed with water, ethanol and dried in vacuum to give white solid.

Part II. Preparation of $[(n\text{-}C_4H_9)_4N]_4$ $[PW_{11}VO_{40}]$

$NaH_2PO_4 2H_2O$ (0.19 g) was added to a solution of 4.12 g of $Na_2WO_4 2H_2O$ in 150 mL water, followed by the addition of 22 mL conc. HCl. After stirring, 5.0 mL V(V) stock solution (prepared by dissolving 6 g NH_4VO_3 and 4 g NaOH in 100 mL water) was added. A solution

of $(n\text{-}C_4H_9)_4NBr$ was added dropwise with stirring after heating at 70°C for 24 h. The precipitates were filtered out, washed with water, ethanol and dried in vacuum at 50°C. The compound was recrystallized from acetonitrile.

Oxidation Process

In a 100 ml flask equipped with a reflux condenser and magnetic stirrer, catalyst and substrate were added. Then 30% H_2O_2 was slowly added and the reaction mixture was stirred at different temperature and time. The mixture was immediately cooled to room temperature. The catalyst was separated by centrifuging. The 25% v/v of H_2SO_4 was added to liquid phase. The reaction products were extracted with diethyl ether. The organic layer was neutralized with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4. Products were determined by GC. Quantification was done by determining the response factors of the reagents and products obtained using standard mixtures.

Results and Discussion

Catalyst Characterization

Compositions of the polyoxotungstates were confirmed by elemental analysis (shown in Table 1). The measured values are in good agreement with the theoretical values.

Table 1 Elemental analyses of polyoxometalates

Catalyst	%P	%W	%V
$[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$ or $(H_{108}C_{48}N_3PW_{12}O_{40})$	0.82 (0.85)	60.56 (61.20)	0
$[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$ or $(H_{144}C_{64}N_4PW_{11}VO_{40})$	0.80 (0.77)	53.85 (54.44)	1.28 (1.37)

Note: Theoretical values are in parentheses.

FT-IR was taken to reveal structure of the catalysts (shown in Table 2). The characteristic peaks are in accordance with the Keggin anionic framework [19]. The major IR peaks are associated with the P-O, $W=O_t$, $W\text{-}O_c\text{-}W$ and $W\text{-}O_e\text{-}W$ (or V) stretching vibrations (t = terminal, c = in corner shared octahedral, e = in edge shared octahedral oxygens). For the V-substituted polyoxometalate, the P-O band split into two bands at 1073 and 1095 cm^{-1}. Since the tetrahedral symmetry around PO_4 is removed by V(V) substitution, the degeneracy is removed [20].

Table 2 FT-IR spectra of polyoxometalates

Catalyst	Wavenumber (cm^{-1})			
	$\upsilon_{as\ P\text{-}O}$	$\upsilon_{as\ W=Ot}$	$\upsilon_{as\ W-Oc-W}$	$u_{as\ W-Oe-W(or\ V)}$
$[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$	1080	978	895	813
$[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$	1073,1095	965	886	809

Figure 2 shows the UV spectra of the $[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$ and $[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$ in acetonitrile. An absorption maximum of the $[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$ appears at 268 nm typical of the Keggin structure. This band is associated with octahedrally coordinated W^{6+} and arises due to ligand to metal charge transition. The presence of vanadium in the Keggin structure of the $[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$ shifted the absorption band to 261 nm.
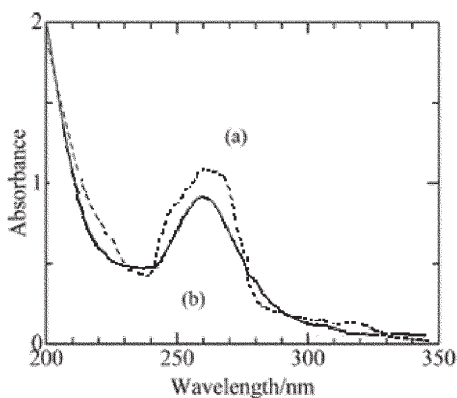

Figure 2. UV spectra of (a) $[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$ and (b) $[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$, in CH_3CN solution.

Oxidation of Cyclohexane and Cyclooctane

The catalysts were tested for their catalytic activities in the oxidation of cyclohexane and cyclooctane using H_2O_2 as an oxidant in the presence or CH_3CN as solvent. The tetrabutyl ammonium salts can dissolve well in CH_3CN which is miscible with water. The reaction conditions and the results are presented in Table 3.

Table 3 Oxidation of cyclohexane and cyclooctane by hydrogen peroxide

Entry	Catalyst	Substrate	Conversion[a] (%)	Selectivity (%)		
				-one	-ol	-OOH
1	No catalyst	cyclohexane	2	49	51	0
2	No catalyst	cyclooctane	2	48	52	0
3	No H_2O_2	cyclohexane	0	0	0	0
4	No H_2O_2	cyclooctane	0	0	0	0
5	$[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$	cyclohexane	51	53	37	10
6		cyclohexane [b]	0	0	0	0
7		cyclooctane	60	54	38	8
8		cyclooctane [b]	0	0	0	0
9	$[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$	cyclohexane	63	52	29	19
10		cyclohexane [b]	0	0	0	0
11		cyclooctane	70	50	30	20
12		cyclooctane [b]	0	0	0	0

Reaction condition: substrate 23 mmol, catalyst 0.05 mmol, H_2O_2/cyclohexane molar ratio = 3, CH_3CN 5 ml, reaction temperature 70°C, time 8 h.

-one = ketone, -ol = alcohol, -OOH = cycloalkyl hydroperoxide

[a]Based on gas chromatographic peak areas.

[b]Experiment carried out with 23 mmol of 2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger.

Reaction control carried out in the absence of catalyst show very low conversion (2%) of cyclohexane and cyclooctane (entries 1-2) whereas the reactions performed in the absence oxidant show no product (entries 3-4). The major oxidized products from the oxidation of cycloalkanes are ketone and alcohol.

For the catalyzed reaction, when oxidation was carried out with vanadium-free polyoxometalate lower activity was observed compared to the vanadium substitu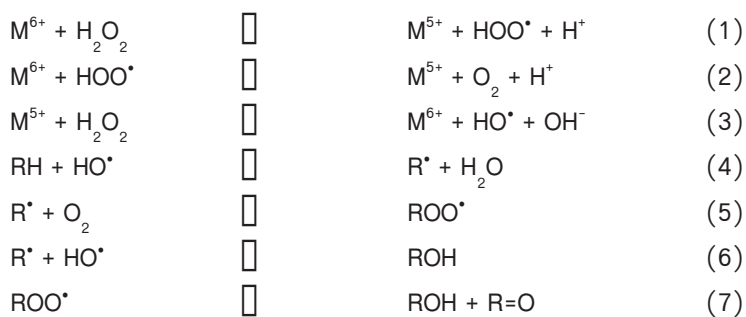ted polyoxometalate catalyst. These results show that the $[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$ is more active than the $[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$ catalyst under the same reaction condition. This reveals the role of vanadium as active center in the oxidation reaction.

As for the product selectivity, both catalysts gave higher selectivity to ketone than alcohol. Cycloalkyl hydroperoxide was also formed. The amount of cycloalkyl hydroperoxide was determined by adding triphenylphosphine (PPh_3) to the reaction products and the GC analysis of this showed a sharp increase in the concentration of cycloalkanol while the concentration

of cycloalkanone substantially reduced. This proves that cycloalkane oxidation proceeds *via* the cycloalkyl hydroperoxide (intermediate) formation, which is found to be reduced by PPh_3. Cycloalkyl hydroperoxide is short lived and gets decomposed in the chromatographic column to yield the corresponding alcohol and ketone. It was found that the $[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$ yielded higher amount of cycloalkyl hydroperoxide than the $[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]$. However, in this work the cycloalkyl hydroperoxide amount is much lower than that reported on oxidation of cyclohexane over $[(n\text{-}C_4H_9)_4N]_4[PW_{11}Fe(H_2O)O_{39}]$ catalyst (80% cyclohexyl hydroperoxide (80%) [21]. In addition, it was reported that cyclooctane oxidation with H_2O_2 in the presence of tetrahexylammonium (THA) salt of the peroxocomplex, $(THA)_2[W_2O_3(O_2)_4]$ and CH_3CN gave rise to cyclooctanone, cyclooctanol and cyclooctyl hydroperoxide in 59:12:29 with 83% conversion under the condition of: catalyst 1.5 mmol, cyclooctane 1 mmol, H_2O_2/cyclooctane molar ratio = 2, reflux temperature; time 12 h [22].

In entries 6, 8, 10 and 12, the reactions were performed with addition of 2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger. The results show that oxidations of cyclohexane and cyclooctane catalyzed by both catalysts appear to be a radical process because no product was detected. The mechanism of the oxidation reaction can be proposed as follows: coordination of H_2O_2 molecule to metal active center $(W^{6+}$ and $V^{5+})$ in the catalyst, resulting in the formation of HOO• followed by O_2 in Eqs. 1-2. The HO• radicals were generated by a reaction in Eq. (3), with re-oxidation of metal. The radicals reacted with substrate (RH) to create R• radical in step (4). The alkyl hydroperoxide ROO• was formed as in step (5). Oxidized products, alcohol (ROH) and ketone (R=O) were produced as in steps (6-7).

$$M^{6+} + H_2O_2 \qquad M^{5+} + HOO^\bullet + H^+ \qquad (1)$$
$$M^{6+} + HOO^\bullet \qquad M^{5+} + O_2 + H^+ \qquad (2)$$
$$M^{5+} + H_2O_2 \qquad M^{6+} + HO^\bullet + OH^- \qquad (3)$$
$$RH + HO^\bullet \qquad R^\bullet + H_2O \qquad (4)$$
$$R^\bullet + O_2 \qquad ROO^\bullet \qquad (5)$$
$$R^\bullet + HO^\bullet \qquad ROH \qquad (6)$$
$$ROO^\bullet \qquad ROH + R{=}O \qquad (7)$$

Oxidation of Alcohols

The oxidation of cyclohexanol and benzyl alcohol was investigated using aq. H_2O_2 as an oxidant under solvent-free condition. Alcohols used here are immiscible with water and hence the present system involves two phases. The results are shown in Table 4. Oxidation products are cyclohexanone and benzaldehyde, respectively. Reaction control carried out in the absence of catalyst shows only 9% of cyclohexanone and

10% conversion of benzaldehyde (entries 1 and 2). Both catalysts show high conversion of alcohol and excellent product selectivity (100%). The replacement of W^{6+} atoms by V^{5+} led to higher conversion of alcohols (entries 3 vs. 6 and entries 5 vs. 8). In this work, we use higher molar ratio of catalyst to substrate (0.002) than that used in our previous work (molar ratio of catalyst to substrate = 0.001) [23] and found that comparable conversions can be obtained in shorter reaction time (3 h) (entries 3 vs. 4 and entries 6 vs. 7).

Table 4 Oxidation of cyclohexanol and benzyl alcohol by hydrogen peroxide

| Entry	Catalyst	Substrate	Product	Conversion [a]	Selectivity
				%	%
1	–	cyclohexanol	cyclohexanone	9	100
2	–	benzyl alcohol	benzaldehyde	10	100
3	$[(n\text{-}C_4H_9)_4N]_3[PW_{12}O_{40}]c$	yclohexanol	cyclohexanone	84	100
4		cyclohexanol [b]	cyclohexanone	82	100
5		benzyl alcohol	benzaldehyde	81	100
6	$[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$	cyclohexanol	cyclohexanone	92	100
7		cyclohexanol [b]	cyclohexanone	93	100
8		benzyl alcohol	benzaldehyde	88	100

Reaction condition: substrate 23 mmol, catalyst 0.05 mmol, H_2O_2/substrate molar ratio = 2, reaction temperature 90°C, time 3 h.

[a]Based on gas chromatographic peak areas.

[b]Reaction condition: substrate 6.7 mmol, catalyst 10 mmol, H_2O_2/substrate molar ratio = 2, reaction temperature 90°C, time 5 h (from ref. 23)

In this work, the reactions were conducted under solvent-free condition. As shown in Scheme 1 the reaction was biphasic system (aqueous and substrate phases), tetrabutylammonium salt can function as a phase transfer catalyst between organic and aqueous phases. In the presence of H_2O_2, the metal in tetrabutylammonium salt is oxidized and dissociated to form peroxometal anion. The substrates are oxidized by peroxometal complex and form oxygenated product. The vanadium in the polyoxometalate establishes a reversible oxidation-reduction. An electron is transferred from the organic substrate to the vanadium-substituted polyoxometalate.
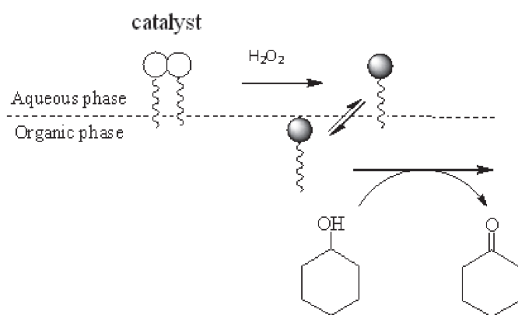
Scheme 1. Phase transfer catalysis mechanism.

For comparison, there was also a work on oxidation of benzyl alcohol over $[C_7H_7N(CH_3)_3]_7PW_{11}O_{39}$ using H_2O_2 as oxidant in the presence of different solvents. The conversion of benzyl alcohol increased with increasing the polarity of the solvents: acetonitrile (70%) < dimethylformamide (84%) with 99% selectivity [11].

We also studied the reusability of the catalyst. The catalyst could be easily recycled by filtration and dried at 100°C for 2 h. Then it was reused with alcohol and hydrogen peroxide as above. It was found that the reaction was carried out at least 3 times in consecutive run with only a slight decrease in activity (Table 5).

Table 5   Reusability of the $[(n-C_4H_9)_4N]_4[PW_{11}VO_{40}]$ catalyst on oxidation of cyclohexanol and benzyl alcohol

Alcohol	No. use	Conversion %	Selectivity %
cyclohexanol	1	92	100
	2	90	100
	3	89	100
Benzyl alcohol	1	88	100
	2	86	100
	3	84	100

Reaction condition: substrate 23 mmol, catalyst 0.05 mmol, H_2O_2/substrate molar ratio = 2, reaction temperature 90°C, time 3 h.

Conclusions

The tetrabutylammonium salts of the Keggin-type polyoxometalates with and without vanadium were synthesized and characterized. They are soluble in CH_3CN solvent. The oxidation of cycloalkanes and alcohols were efficiently done using environmental friendly oxidant, H_2O_2. The cyclohexane and cyclooctane were oxidized to the corresponding ketone and alcohol with high conversion (51-70%) and high selectivity to ketone (50-54%) at 70°C in 8 h. Both cyclohexanol and benzyl alcohol can be oxidized at 90°C in 3 h with excellent product selectivity (100%) in the absence of any added solvent. The tetrabutylammonium ion acted as phase transfer agent. The vanadium(V)-substituted polyoxometalate was shown to be more active catalyst than the unsubstituted polyoxometalate and It can also be reused 3 times.

References

[1]　Sato, K., Aoki, M., Takagi, J., Notori, R. (1997). Organic Solvent- and Halide-Free Oxidation of Alcohols with Aqueous Hydrogen Peroxide. *Journal of American Chemical Society.* 119: 12386-12387.

[2]　Shylesh, S., Samuel, P. P., Singh, A. P. (2007). Chromium-containing Small Pore Mesoporous Silicas: Synthesis, Characterization and Catalytic Behavior in the Liquid Phase Oxidation of Cyclohexane. *Applied Catalysis A: General.* 318: 128-136.

[3]　Kuznetsova, L. I., Kuznetsova, N. I., Detusheva, L. G., Fedotov, M. A., Likholobov, V. A. (2000). Active Metal Species Assembled with Heteropoly Tungstate Anion $PW_9O_{34}{}^9$ for Liquid Phase Hydrocarbon Oxidation. *Journal of Molecular Catalysis A: Chemical.* 158: 429-433.

[4]　Noritaka, M., Nozaki, C., Kiyoto, I., Misono, M. (1998). Highly Efficient Utilization of Hydrogen Peroxide for Selective Oxygenation of Alkanes Catalyzed by Diiron-Substituted Polyoxometalate Precursor. *Journal of American Chemical Society.* 120: 9267-9272.

[5]　Kuznetsova, G. L.Semin, F. Cavani, F. Trifir. (1997). Reactivity of Transition-metal-modified, Keggin-type Heteropoly Complexes in the Homogeneous Oxidation of Cyclohexane and Adamantane. *Journal of Molecular Catalysis A: Chemical.* 127: 85-94.

[6]　Sheldon, R. A., Arends, I. W. C. E., Dijksman, A. (2000). New Developments in Catalytic Alcohol Oxidations for Fine Chemicals Synthesis. *Catalysis Today.* 57: 157-166.

[7]　Yang, J. I., Lee, D., Lee, J., Hyun, J. C., Lee, K. (2000). Selective and High Catalytic Activity of $Mo_{11}VO_{40}$ (n= 3) for Oxidation of Ethanol. *Applied Catalysis A: General.* 123: 194-200.

[8]　Wang, J., Yan, L., Li, G., Wang, X., Ding, Y., Suo, J. (2005). Polyoxometalate Compound: a Highly Efficient Heterogeneous Catalyst for Aerobic Alcohol Oxidation. *Tetrahedron Letter.* 46: 7023-7027.

[9]   Kato, C. N., Shinohara, A., Moriya, N., Nomiya, K. (2006). Water-soluble Organometallic Ruthenium(II) Complexes Supported on Dawson-type Polyoxotungstates as Precatalysts: Selective Oxidation of Alcohols with 1 atm Molecular Oxygen. *Catalysis Communications.* 7: 413–416.

[10] Hill, C. L., Prosser-McCartha, C. M. (1995). Homogeneous Catalysis by Transition Metal Oxygen Anion Clusters. *Coordination Chemistry Reviews.* pp. 143–151.

[11] Weng, Z., Wang, J., Jian, X. (2008). A Reusable and Active Lacunary Derivative $[PW_{11}O_{39}]^{7-}$ as Benzyl Alcohol Oxidation Catalyst with Hydrogen Peroxide. *Catalysis Communications.* 9: 1688–1693.

[12] Zhang, S., Zhao, G., Gao, S., Xi, Z., Xu, J. (2008). Secondary Alcohols Oxidation with Hydrogen Peroxide Catalyzed by $[n\text{-}C_{16}H_{33}N(CH_3)_3]_3PW_{12}O_{40}$: Transform-and-retransform Process between Catalytic Precursor and Catalytic Activity Species. *Journal of Molecular Catalysis A: Chemical.* 289: 22-27.

[13] Khenkin, A. M., Leitus, G., Neumann, R. (2008). Electron Transfer-Oxygen Transfer Oxygenation of Sulfides Catalyzed by the $H_5PV_2Mo_{10}O_{40}$ Polyoxometalate. *Journal of American Chemical Society.* 130: 14474–14476.

[14] Kozhevnikov, I. V. (1998). Heteropolyacids and Related Compounds as Catalysts for Fine Chemical Synthesis. *Catalysis Reviews: Science Engineering.* 37: 311-316.

[15] Nomiya, K., Yagishita, K., Nemoto, Y., Kamataki, T. (1997). Functional Action of Keggin-type Mono-vanadium(V)-substituted Heteropolymolybdate as a Single Species on Catalytic Hydroxylation of Benzene in the Presence of Hydrogen Peroxide. *Journal of Molecular Catalysis A: Chemical.* 126: 43-53.

[16] Misono, M., Mizuno, N., Inumaru, K., Koyano, G., Lu, X-H. (1997). Selective oxidation of hydrocarbons catalyzed by heteropoly compounds. *Studies in Surface Science and Catalysis.* 110: 35-42.

[17] Trakarnpruk W, Rujiraworawut K. (2009). Oxidative Desulfurization of Gas oil by Polyoxometalates Catalysts. *Fuel Processing Technology.* 90: 411-414.

[18] Dewan, A., Sarma, T., Bora, U., Kakati, D. K. (2011). Rapid and Selective Oxidation of Benzyl Alcohols to Aldehydes and Ketones with Novel Vanadium Polyoxometalate under Solvent-free Conditions. *Tetrahedron Letters.* 52: 2563-2565.

[19] Deltcheff, C., Fournier, M., Franck, R., Thouvenot, R. (1983). Vibration Investigations of Polyoxometalates. 2. Evidence for Anion-anion Interactions in Molybdenum (VI) and Tungsten (VI) Compounds Related to Keggin Structure. *Inorganic Chemistry.* 22: 207-216.

[20] Ueda, T.; Komasu, M.; Hojo, M. (2003). Spectroscopic and Voltammetric Studies on the Formation of Keggin type V(V)-substituted Tungstoarsenate (V) and –phosphate (V) Complexes in Aqueous and Aqueous-organic Solutions. *Inorganic Chimica. Acta.* 344: 77-84.

[21] Balulaa, M. S., Santosa, I. C. M. S., Simoes, M. M. Q., Grac M., Neves, P. M. S., Cavaleiro, J. A. S., Cavaleiro, A. M. V. (2004). A Comparative Study between Keggin-type Tungstophosphates and Tungstosilicates in the Oxidation of Cyclooctane with Hydrogen Peroxide. *Journal of Molecular Catalysis A: Chemical.* 222 (2004): 159-165.

[22] Santos, I. C. M. S., Paz, F. A. A., Simoes, M. M. Q., Grac M., Neves, P. M. S., Cavaleiro, J. A. S., Klinowski, J., Cavaleiro, A. M. V. (2008). Catalytic Homogeneous Oxyfunctionalization with Hydrogen Peroxide in the Presence of a Peroxotungstate. *Applied Catalysis A: General.* 351: 166-173.

[23] Kanjina, W., Trakarnpruk, W. (2009). Heteropolyoxometalate Catalysts for Selective Oxidation of Alcohols with H_2O_2. *Silpakorn University Science and Technology Journal (SUSTJ).* 3(1): 7-12.