International Journal of Chemical Engineering and Applications, Vol. 6, No. 2, April 2015

Heterogeneous Catalytic Oxidation of Cyclohexane with H_2O_2 Catalyzed by Cs- and TBA-salts of Cu- and Mn-Polyoxotungstates on MCM-41

W. Trakarnpruk

***Abstract*—Cs-and tetrabutyl ammonium (TBA) salts of Cu- and Mn-polyoxotungstates were synthesized. They were loaded on MCM-41 support (by impregnation method in 20-30 wt%) to increase surface area of the catalysts. The supported catalysts were characterized by inductive coupled plasma emission (ICP), Fourier-Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD) and nitrogen adsorption-desorption. Their catalytic activities for oxidation of cyclohexane were compared using green oxidant H_2O_2 under mild reaction conditions. The oxidized products are cyclohexanol and cyclohexanone. The activities follow the order: TBA-CuPOM/MCM > TBA-MnPOM/MCM > Cs-CuPOM/MCM > Cs-MnPOM/MCM. The Mn containing catalysts gave higher cyclohexanone selectivity than Cu containing catalysts. The Cs salt catalysts can be reused without loss of activity due to its insolubility in the reaction medium. The 30wt%Cs-CuPOM/MCM and 30wt% Cs-MnPOM/MCM gave comparable activity (16-17 % conversion with 75-76 %selectivity using H_2O_2/cyclohexane mole ratio = 4 at 80 ˚C in 12 h. The oxidation reaction appears to be radical process, since it was inhibited in the presence of radical scavenger.**

***Index Terms*—Polyoxotungstate, cyclohexane, oxidation, MCM-41.**

I. INTRODUCTION

The oxidation of cyclohexane is an important industrial process. The cyclohexanone and cyclohexanol products are intermediates in nylon manufacture that uses homogeneous Co species as catalysts and O_2 as oxidant, to give e.g. cyclohexanone (80% selectivity, ca. 4% conversion), at a considerably high temperature (150 ˚C) and pressure (15 bar) [1]. Catalytic oxidation of cyclohexane have been carried out using a variety of oxidants such as iodosylbenzene [2], alkyl hydroperoxides [3], *m*-chloroperbenzoic acid [4] and oxygen [5]. Molecular oxygen is possibly the best oxidant choice. However, non-selective radical-chain reactions usually occur. Hydrogen peroxide is an interesting alternative to O_2, due to its high 47% active oxygen content, availability and relatively low price, and to the fact of giving environmentally benign water as by-product.

Transition metal-substituted polyoxotungstates $[PMW_{11}O_{39}]^{(n-m)-}$ in which a transition metal cation, M^{m+}, is coordinated to the binding sites of lacunary heteropolyanions $[PW_{11}O_{39}]^{n-}$ (see Fig. 1), have attracted interest as catalysts in many reactions because of their thermal and chemical stability and the possibilities for modification.They bear many similarities to metal complexes of macrocyclic ligands and metalloporphyrins because they possess rigid co-ordination sites surrounding a metal centre [6]. With d^0 electronic configuration of tungsten(VI) species, they do not cause excessive catalytic dismutation of hydrogen peroxide [7]. They have been used as oxidative catalysts in many reactions [8], [9]. Tetrabutylammonium (TBA) salts of polyoxotungstates are soluble in organic solvent, they can be transferred from aqueous phase into weak polar or non-polar organic phase allowing good contact between the organic substrates with the catalytic active species [10]. Balulu *et al.* reported catalytic activities of the $(TBA)_4[PW_{11}M(H_2O)O_{39}].2H_2O$ (M = Fe, Mn, and V) in oxidation of cyclooctane with H_2O_2 [11]. Simoes *et al.* studied activity of $(TBA)_4[PW_{11}Fe(H_2O)O_{39}]$ in oxidation of cyclohexane with H_2O_2 and found high selectivity to cyclohexyl hydroperoxide. They also compared catalytic activity of the TBA salts in which M = Cu, Co, Mn, and Ni in one reaction condition [12]. In previous papers, I reported on the catalytic behaviour of $(TBA)_4HPW_{11}Co(H_2O)O_{39}$ in oxidation of cyclohexane and ethylbenzene [13] as well as TBA salts of Co, Fe, Cu and V polyoxotungstates supported on MCM-41 for oxidation of cyclohexane and cyclooctane using H_2O_2 [14].

The application of polyoxometalate has been restricted by the low surface. It was reported that its Cs salt has high surface area and is water-tolerant [15]. However the Cs salt disperses as a colloid in water and organic solvents, making it difficult to separate from the reaction products. One way to solve this problem is to disperse it on a carrier with a high specific surface area. The heterogenization of homogeneous catalysts has been an important tendency in catalysis research. Advantages are easiness of recovery and recycling after carrying out liquid phase reactions, and the easier product isolation, compared to that of the homogeneously catalyzed reactions. Estrada *et al.* reported activity of $(TBA)_4PW_{11}FeO_{39}$ on triethylpropylammonium -functionalized silica in catalytic oxidation of cyclooctane using H_2O_2 as oxidant and CH_3CN as solvent. They found that products selectivity (40% cyclooctanone and 38% cyclooctyl hydroperoxide) is different from that obtained in homogeneous system (26% cyclooctanone and 74% cyclooctyl hydroperoxide) at 80 ˚C in 6 h [16].

In this work MCM- 41 support was chosen as support due to its hydrophobicity, high surface area, uniform and controllable pore sizes and the periodic orders of their pore

---

Manuscript received February 24, 2014; revised July 1, 2014.

Wimonrat Trakarnpruk is with the Department of Chemistry, Faculty of Science, Chulalongkorn University, Thailand (e-mail: wimonrat.t@chula.ac.th).

DOI: 10.7763/IJCEA.2015.V6.464

packing which provides a tremendous dispersion of the active species over it. I present reactivity of TBA and Cs salts of Cu- and Mn-substituted polyoxotungstates immbolized in MCM-41 for oxidation of cyclohexane using a clean oxidant H_2O_2.

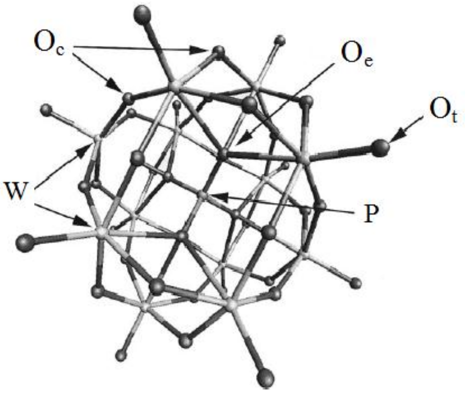


Fig. 1. Structure of Keggin polyoxotungstate.

II. EXPERIMENTAL METHODS

A. Catalysts Preparation and Characterization

The following commercially available reagents were used without further purification: Na_2HPO_4, $Na_2WO_4.2H_2O$, $Cu(NO_3)_2.3H_2O$, $MnCl_2.4H_2O$, Cs_2CO_3, tetrabutylammonium bromide (CTABr) (Fluka); $H_3PW_{12}O_{40}.3H_2O$ (Aldrich), acetonitrile (Lab-Scan); H_2O_2 (30 wt% aqueous), cyclohexane, cyclohexanone, cyclohexanol and 2,6-di-*tert*-butyl-4-methylphenol (Merck).

1) Preparation of polyoxotungstates

a) Tetrabutyl ammonium salts, TBA-Cu(or Mn)POM

Tetrabutyl ammonium salts were synthesized following the procedure described [12]: Na_2HPO_4 (9.1 mmol), $Na_2WO_4.2H_2O$ (100 mmol) and $Cu(NO_3)_2.3H_2O$ or $MnCl_2.4H_2O$ (12 mmol) were dissolved in 200 mL of water. The pH of the solution was adjusted to 4.8. An aqueous solution of tetrabutylammonium bromide (45 mmol) in 20 mL was added dropwise, while stirring at 80 ˚C. The solid was filtered off, washed and dried in vacuum at 50 ˚C. The compounds were recrystallized from acetonitrile. The chemical composition was confirmed by ICP (Perkin Elmer Plasma 1000 Emission Spectrometer), in agreement with the literature.

$[(n\text{-}C_4H_9)_4N]_4HPW_{11}Cu(H_2O)O_{39}$ or TBA-CuPOM. Anal. Found: W, 54.8; P, 0.79; Cu, 1.59; Calculated: W, 54.5; P, 0.83; Cu, 1.71 %.

$[(n\text{-}C_4H_9)_4N]_4HPW_{11}Mn(H_2O)O_{39}$ or TBA-MnPOM. Anal. Found: W, 52.1; P, 0.86; Mn, 1.25; Calculated: W, 53.6; P, 0.82; Mn, 1.46 %.

b) Sodium salts, Na- Cu (or Mn)POM

Sodium salt of polyoxotungstates were synthesized following the procedure described by Rana *et al.*: $H_3PW_{12}O_{40}$ (2.88 g, 1 mmol) was dissolved in 10 ml water and the pH of the solution was adjusted to 4.8 using $NaHCO_3$ solution. The solution was heated to 90 ˚C and a solution of $Cu(NO_3)_2.3H_2O$ or $MnCl_2.4H_2O$ (1 mmol) in 10 ml water was added. The solvent was evaporated, the solid was recrystallized from water and dried.

2) Preparation of support and supported catalysts

a) MCM-41

MCM-41 was prepared with a composition of SiO_2:CTABr:NH_4OH:H_2O = 1.0:0.12:8:114 or 26 ml: 5 g: 57 ml: 235 g. Ammonia and CTABr were dissolved in deionized water. TEOS was then added dropwise. After 2 h stir, a gel was formed. It was heated at 110 ˚C for 96 h in a Teflon bottle. The solid was recovered by filtration, washed with deionized water and dried. The template was removed by extracting the product in a refluxing acidic methanol.

b) TBA-Cu (or Mn)POM/MCM

The supported catalyst was prepared by incipient wetness impregnation method. The calculated amount of TBA-Cu (or Mn)POM (20 and 30 wt.% based on MCM-41) was dissolved in 5 ml CH_3CN and were added onto 1 g MCM-41. The mixture was stirred for 3 h at 80 ˚C. The solvent was evaporated and the solid was calcined at 350 ˚C for 3 h.

c) Cs-Cu (or Mn)POM/MCM

The catalysts were prepared by two-step incipient wetness impregnation method. MCM-41 (1 g) was first impregnated with Cs_2CO_3 (10 mg, 0.03 mmol or 20 mg, 0.06 mmol), in 10 ml water, the mixture was stirred for 12 h. Then it was dried at 110 ˚C and calcined at 350 ˚C for 3 h. Then the calculated amount of Na-Cu (or Mn)POM (20 wt% which is approximately 0.07 mmol, and 30 wt% which is approximately 0.10 mmol) in 10 ml water was added. The mixture was stirred for 12 h. The product was dried and calcined at 350 ˚C for 3 h. Cs content was confirmed by ICP. All supported catalysts were analyzed by FTIR (Nicolet FTIR Impact 410 Spectro-photometer), BET (BELSORP-mini) and XRD (Rigaku, DMAX 2002/Ultima Plus powder X-ray diffractometer).

B. Oxidation Reactions with Hydrogen Peroxide

The reactions were typically carried out in a Parr reactor. Cyclohexane (92 mmol, 10 ml), catalyst and 30% H_2O_2 were mixed in 10 ml CH_3CN. The reaction was conducted at 80 ˚C. After required time, the catalyst was separated, and the products were extracted with diethyl ether and dried. Each compound in the reaction mixture was analyzed using a Shimadzu model CG-17A equipment with flame ionization detector and OV-1701 0.50 μm capillary column (30 m, 0.25 mm), and *n*-octane as internal standard. The chromatographic conditions was: initial temperature 80 ˚C (4 min); temperature rate 15˚C/min; final temperature 200˚C (3 min); injector temperature 180˚C and detector temperature 180˚C. Quantification was done by determining the response factors of the reagents and products obtained using standard mixtures. Blank reactions without catalyst were performed in all conditions studied. No oxidation products were detected.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

The textural properties such as BET surface area, pore diameter and pore volume derived from the N_2 adsorption-desorption measurements are included in Table I. Loading the TBA or Cs salts of Cu- (or Mn)POM to the support brings about a certain decrease in the BET surface areas. The resulting supported samples, nevertheless, still have high enough surface area to ensure the formation of well-dispersed catalytic materials. The pore volume and pore size of the supported catalysts are smaller than that of MCM-41. Adsorption isotherms of the supported catalysts could be assigned to type IV isotherm. There is a drop in the adsorption condensation region, at p/p_0 = 0.3-0.4. It is expected that POM species occupied and dispersed on MCM-41 surface causes the drop in the adsorption region.

The amount of POM in the supported catalysts was measured in terms of tungsten percentage as obtained from ICP results. Table I also shows that % POM analyzed is a little lower than the loading value. The Cs:W ratio is in range of 1.5-1.7:12.

TABLE I: CHEMICAL ANALYSIS, TEXTURAL PARAMETERS OF CATALYSTS

Catalyst	Anal[a] (%)	Cs:W ratio[b]	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
MCM	0	-	1040	0.80	2.97
20TBA-CuPOM/MCM	19.3	-	715	0.42	2.70
30TBA-CuPOM/MCM	29.4	-	592	0.39	2.60
20TBA-MnPOM/MCM	19.4	-	704	0.41	2.67
30TBA-MnPOM/MCM	29.6	-	556	0.38	2.57
20Cs-CuPOM/MCM	19.1	1.5:12	721	0.58	2.30
30Cs-CuPOM/MCM	29.2	1.6:12	703	0.55	2.21
20Cs-MnPOM/MCM	19.3	1.6:12	717	0.57	2.28
30Cs-MnPOM/MCM	29.5	1.7:12	700	0.56	2.20

[a]Deduced from the chemical analysis of W by ICP
[a]Deduced from the chemical analysis of Cs and W by ICP

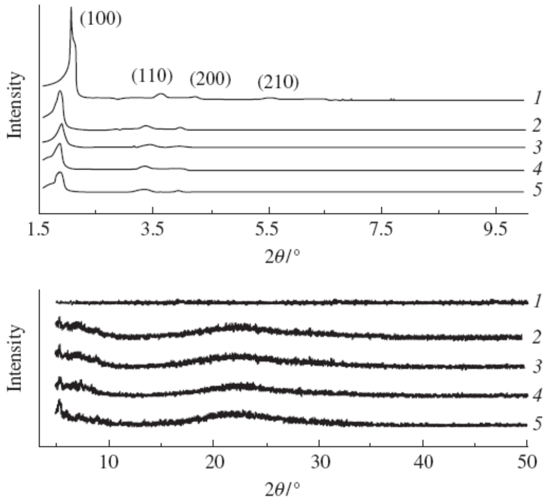


Fig. 2. XRD patterns in low angle and wide angles of *(1)* MCM-41, *(2)*, *(3)* 20TBA Cu- and MnPOM/MCM, *(4)*,*(5)* 30TBA- Cu- and MnPOM/MCM.

The powder XRD patterns of the MCM-41 exhibits a low-angle diffraction peak correspond to the (100), (110) (200) and (210) planes. The 100 diffraction of the MCM-41 is still observed after the POM loading although the intensity of the diffraction peak becomes broader and weaker as the POM loadings increases. Representative XRD patterns showing low and wide angle regions of TBA-CuPOM/MCM and TBA-MnPOM/MCM are shown in Fig. 2. The patterns show a broad peak without characteristic peaks of polyoxotungstate, indicating high dispersion of polyoxotungstate in a non-crystalline form on the surface of MCM-41. However for the XRD patterns of the Cs-CuPOM/MCM and Cs-MnPOM/MCM (Fig. 3), in case of the 30 wt% loading little peaks of the crystalline polyoxotungstate can be observed.

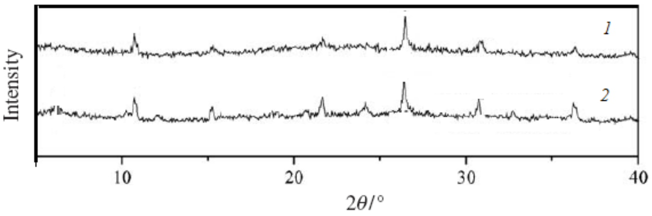


Fig. 3. XRD patterns (wide angle) of *(1)* 30Cs-CuPOM/MCM and *(2)* 30Cs-MnPOM/MCM.

The FT-IR spectra of TBA-CuPOM, MCM-41 and 30TBA-CuPOM/MCM are shown in Fig. 4. Other catalysts have similar spectra. The existence of POM on the support was confirmed by a tiny band at 887 cm^{-1}. Other catalysts show similar spectra. However other bands of TBA-POM (in Table II) are not clearly evident as well as the bands attributed to ν_{as}(P-O) vibration were obscured by an intense and broad band of MCM-41.

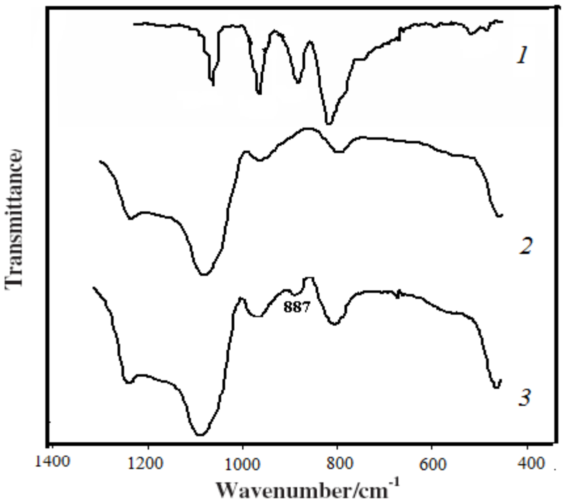


Fig. 4. FTIR spectra of *(1)* TBA-CuPOM, *(2)* MCM and *(3)* 30TBA-CuPOM/MCM.

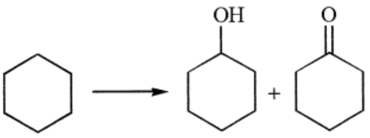
TABLE II: FTIR FREQUENCIES (CM^{-1}) OF POM

Catalyst	W-O_e-W	W-O_c-W	W=O_t	P-O
TBA-MnPOM	818	887	967	1057, 1073
TBA-CuPOM	816	888	964	1067,1101

O_e (edge share), O_c (corner share), O_t (terminal)

B. Cyclohexane Oxidation

The oxidation of cyclohexane was performed over 20TBA-CuPOM/MCM with H_2O_2 in CH_3CN at 80 ˚C to study various parameters influencing the reaction such as H_2O_2/cyclohexane mole ratio, catalyst amount and reaction time. Results are shown in Table III. The oxidized products are cyclohexanol (CyOH) and cyclohexanone (CyONE), as in (1). In this work cyclohexyl hydroperoxide was not detected from the reaction. The absence of cyclohexyl hydroperoxide was confirmed by reducing it with triphenylphosphine to cyclohexanol [17]. No increase in cyclohexanol was detected.



(1)

In Table III increasing the H_2O_2/cyclohexane mole ratio from 2 to 4, the conversion improved. By increasing the amount of catalyst from 0.4 g to 0.6 g, which results in an increase of the active sites, an increase in conversion was obtained. As for the selectivity, it was increased by increasing H_2O_2/cyclohexane mole ratio or reaction time. Using 0.6 g catalyst, H_2O_2/cyclohexane mole ratio = 4 and 12 h reaction time, the catalyst gave 20 % conversion and 73 %cyclohexanone selectivity. When reaction was prolonged to 15 h, no further increase in both conversion and selectivity was obtained. Therefore this condition is chosen for further experiments over TBA-MnPOM/MCM and Cs salts of MnPOM and CuPOM catalysts with 20 and 30 wt% loadings (shown in Fig. 5).

TABLE III: CYCLOHEXANE OXIDATION OVER 20TBA-CUPOM/MCM

Catalyst (g)	H_2O_2/Cy mole ratio	time (h)	Conv.^{a} (%)	Sel.^{b} (%)	
				CyONE	CyOH
0.4	2	6	5	50	40
0.4	3	6	9	65	35
0.4	4	6	14	67	33
0.6	4	12	20	73	27
0.6	4	15	20	73	27

Reaction conditions: cyclohexane 92 mmol (10 ml), CH_3CN 10 ml, 80 ˚C
Cy = cyclohexane, CyONE = cyclohexanone, CyOH = cyclohexanol
^{a}Based on substrate
^{b}Based on the gas chromatographic peak areas.

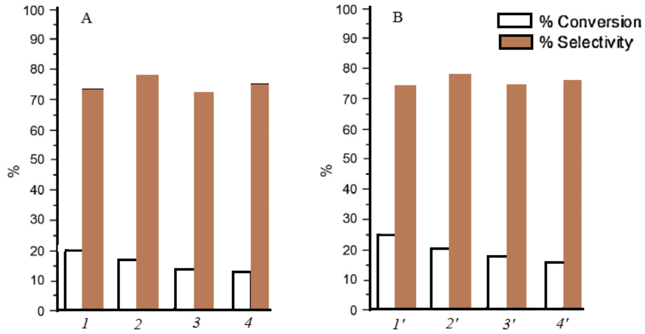


Fig. 5. Conversion and cyclohexanone selectivity of (A) 20 wt% and (B) 30 wt% loading catalysts: *(1),(1')* TBA-CuPOM/MCM *(2),(2')* TBA-MnPOM/MCM *(3),(3')* Cs-CuPOM/MCM, *(4),(4')* Cs-MnPOM/MCM.
(Reaction conditions: cyclohexane 92 mmol, CH_3CN 10 ml, 0.6 g catalyst, H_2O_2/cyclohexane mole ratio = 4, 12 h and 80 ˚C)

In Fig. 5(A) under the same reaction condition, among the 20 wt% loading catalysts, % conversion is in order of: TBA-CuPOM/MCM (20) > TBA-MnPOM/MCM (17)> Cs-CuPOM/MCM (14) > Cs-MnPOM/MCM (13). As for cyclohexanone selectivity the order is: TBA-MnPOM/MCM (77) > Cs-MnPOM/MCM (76) > TBA-CuPOM/MCM (73) > Cs-CuPOM/MCM (72). When the loading is increased to 30 wt% (Fig. 5(B), I obtain enhancement in %conversion: TBA-CuPOM/MCM (25) > TBA-MnPOM/MCM (20)> Cs-CuPOM/MCM (17) > Cs-MnPOM/MCM (16). The order of activity and selectivity from 20wt% and 30 wt% loading catalysts are similar.

For comparison, in homogeneous system Simoes *et al.* reported 11% conversion and 36 %cyclohexanone selectivity with TBA-CuPOM and 8% conversion and 62 %selectivity with TBA-MnPOM (H_2O_2/cyclohexane mole ratio = 1.6-2, in CH_3CN, 80˚C and 12 h) [12].The supported catalysts in this work show higher cyclohexanone selectivity, when compared to the homogeneous ones. This reveals the ability of solid matrices, MCM-41 to control surface reactions modifying the adsorption-desorption equilibria of reagents, reaction intermediates and products. The polar surface of the siliceous support is expected to favor the accumulation of produced alcohols at the interfaces and, consequently, oxidation to ketones.

The catalyst activity could be due to activation of H_2O_2 which may occur simultaneously at W and Cu(Mn). The difference in activity is governed by reduction potential of metals used for substitution. Gamelas *et al.* studied cyclic voltamogram of the TBA-CuPOM. The peaks at less negative potentials were attributed to reduction processes at the Cu atom and the peak at more negative potential was from W [18]. Zhang *et al.* oxidized TBA-MnPOM electrochemically and proposed that in the electrooxidation the corresponding Mn(II) is oxidized to Mn(IV) [19]. Rath *et al.* reported that $Cu_xH_{3-2x}PW_{12}O_{40}$/MCM-41 is more easily reducible than the unsupported one [20].

C. Reusability of Catalyst

The challenge of using solid catalysts in a liquid-phase reaction is their ease of separation and reusability, therefore the recycling of the catalyst has been investigated. At the end of the reaction, the solid catalysts was filtered off and reused. The spent catalysts were analyzed for W content. The analysis data show that the W% in the catalyst dramatically decreases in case of the TBA salts with 30 wt% loading whereas the Cs salts show a slight loss due to its insolubility (shown in Table IV). A similar result showing the heterogeneity of the Cs salt catalyst was also reported for Cs-FePOM/MCM in oxidation of trans-styrene [21].

When the Cs salt catalysts were reused, their activity dropped slightly after the third run but the TBA salt catalysts showed a large decrease in activity. The conversion of the 20 and 30 % loadings dropped from 17-20 to 16-18% conversion and from 20-25 to 17-18 % conversion, respectively. It can be concluded that the Cs salt catalysts exhibit better reusability than the TBA salt catalysts.

TABLE IV: ANALYSIS OF %W

Catalyst	%W (analyzed)	
	Before reaction	After reaction
20TBA-CuPOM/MCM	19.3	18.1
30TBA-CuPOM/MCM	29.4	20.3
20TBA-MnPOM/MCM	19.4	18.0
30TBA-MnPOM/MCM	29.6	19.9
20Cs-CuPOM/MCM	19.1	18.9
30Cs-CuPOM/MCM	29.2	28.5
20Cs-MnPOM/MCM	19.3	19.0
30Cs-MnPOM/MCM	29.5	29.1

D. Reaction Mechanism

In order to prove whether the oxidation reaction occurs via radical pathway, the reaction was performed in the presence of radical scavenger, 2,6-di-*tert*-butyl-4methylphenol. The results show that no reaction products were detected, suggesting the involvement of a radical-chain mechanism in the oxidation of cyclohexane. The mechanism proposed for the oxidation of cycloalkanes with H_2O_2 over the polyoxometalates [11] applies to these catalysts. The metal-catalyzed hemolytic decomposition of H_2O_2 to radicals $HO^\bullet$ and $HOO^\bullet$ can account for the formation of alkyl radical $R^\bullet$ upon H-abstraction from the substrate RH by $HO^\bullet$. Reaction of alkyl radical $R^\bullet$ with metal-peroxide resulted in final oxidized products, cyclohexanone and cyclohexanol.

REFERENCES

[1] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinace, and E. L. Pires, "Cyclohexane oxidation continues to be a challenge," *Appl. Catal. A: Gen*, vol. 211, pp. 1-17, 2001.

[2] D. Mansuy, J. F. Bartoli, P. Battioni, D. K. Lyon, and R. G. Finke, "Highly oxidation resistant inorganic-porphyrin analogue polyoxometalate oxidation catalysts. 2. Catalysis of olefin epoxidation and aliphatic and aromatic hydroxylations starting from α_2-$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{(n-11)}$ (M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+})," *J. Am. Chem. Soc*., vol. 113, pp. 7222-7226, 1991.

[3] Y. Matsumoto, M. Asami, M. Hashimoto, and M. Misono, "Alkane oxidation with mixed addenda heteropoly catalysts containing Ru(III) and Rh(III)," *J. Mol. Catal. A: Chem*., vol. 114, pp. 161-168, 1996.

[4] W. Nam, S. J. Yang, and H. Kim, "Catalytic oxygenation of alkenes and alkanes by oxygen donors catalyzed by cobalt-substituted polyoxotungstate," *Bull. Korean Chem. Soc*., vol. 17, pp. 625-630, 1996.

[5] N. Mizuno, "Synthesis of di-iron-containing inorganic synzyme, γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$, and the liquid-phase oxidation catalysis," *Catal. Surv. Jpn*., vol. 4, pp. 149-154, 2000.

[6] C. L. Hill and C. M. Prosser-McCartha, "Homogeneous catalysis by transition metal oxygen anion clusters," *Coord. Chem. Rev*., vol. 143, pp. 407-455, 1995.

[7] H. Rohit, N. K. Ingle, and K. Raj. "Lacunary Keggin type polyoxotungstates in conjunction with a phase transfer catalyst: An effective catalyst system for epoxidation of alkenes with aqueous H_2O_2," *J. Mol. Catal. A: Chem*., vol. 294, pp. 8-13, 2008.

[8] M. Q. Mário, I. C. M. S. Simoes, M. Santos, S. Salete, S. Balula, J. A. F. Gamelas, A. M. V. Cavaleiro, M. Graça, P. M. S. Neves, and J. A. S. Cavaleiro, "Oxidation of cycloalkanes with hydrogen peroxide in the presence of Keggin-type polyoxotungstates," *Catal. Today*, vol. 91-92, pp. 211-214, 2004.

[9] S. Pathan and A. Patel, "Solvent free clean selective oxidation of alcohols catalyzed by mono transition metal (Co, Mn, Ni)-substituted Keggin-phosphomolybdates using hydrogen peroxide,"*Appl. Catal. A: Gen.*, vol. 459, pp. 59-64, 2013.

[10] R. Ishimoto, K. Kamata, and N. Mizuno, "A highly active protonated tetranuclear peroxotungstate for oxidation with hydrogen peroxide," *Angew. Chem. Int. Ed*., vol. 51, pp. 4662-4665, 2012.

[11] M. S. S. Balula, I. C. M. S. Santos, M. M. Q. Simoes, M. Grac ¸P. M. S. Neves, J. A. S. Cavaleiro, and A. M. V. Cavaleiro, "A comparative study between Keggin-type tungstophosphates and tungstosilicates in the oxidation of cyclooctane with hydrogen peroxide," *J. Mol. Catal. A: Chem*., vol. 222, pp. 159-165, 2004.

[12] M. M Q. Simoes, C. M. M. Conceição, J. A. F. Gamelas, P. M. D. N. Domingues, A. M. V. Cavaleiro, J. A. S. Cavaleiro, A. J. V. Ferrer-Correia, and R. A. W. Johnstone, "Keggintype polyoxotungstates as catalysts in the oxidation of cyclohexane by dilute aqueous hydrogen peroxide," *J. Mol. Catal. A: Chem*., vol. 144, pp. 461-468, 1999.

[13] W. Kanjina and W. Trakarnpruk, "Oxidation of cyclohexane and ethylbenzene by hydrogen peroxide over Co-substituted heteropolytungstate catalyst," *J. Metal, Materials and Minerals Res*., vol. 20, no. 2, pp. 29-34, 2010.

[14] J. Jatupisarnpong and W. Trakarnpruk, "Transition metal-substituted polyoxometalates supported on MCM-41 as catalysts in the oxidation of cyclohexane and cyclooctane with H_2O_2," *Mendeleev Commun.*, vol. 22, pp. 152-153, 2012.

[15] X. Li, Z. Jing, W. Ji, Z. Zhang, Y. Chen, C. Au, S. Han, and H. Hibst, "Effect of vanadium substitution in the cesium salts of Keggin-type heteropolyacids on propane partial oxidation," *J. Catal*., vol. 237, pp. 58-66, 2005.

[16] A. C. Estrada, I. C. M. S. Santos, M. M. Q. Simoes, M. Grac, P. M. S. Neves, J. A. S. Cavaleiro, and A. M. V. Cavaleiro, "Silica supported transition metal substituted polyoxotungstates: Novel heterogeneous catalysts in oxidative transformations with hydrogen peroxide," *Appl. Catal. A: Gen*., vol. 392, pp. 28-35, 2011.

[17] G. B. Shul'pin, "Metal-catalyzed hydrocarbon oxygenations in solutions: The dramatic role of additives: A review," *J. Mol. Catal. A: Chem.*, vol. 189, pp. 39-66, 2002.

[18] J. A. F. Gamelas, M. S. Balula, H. M. Carapuc, and A. M. V. Cavaleiro. "Unusual electrochemical reduction of copper(II) to copper(I) in polyoxotungstates," *Electrochem. Commun*., vol. 5, pp. 378-382, 2003.

[19] X. Y. Zhang, M. T. Pope, M. R. Chance, and G. B. Jameson, "High-valent manganese in polyoxotungstates-1. Manganese(IV) keggin derivatives," *Polyhedron*, vol. 14, pp. 1381-1392, 1995.

[20] D. Rath, S. Rana, and K. M. Parida, "$Cu_xH_{3-2x}PW_{12}O_{40}$ supported on MCM-41: Their activity to Heck vinylation of aryl halides," *Ind. Eng. Chem. Res*., vol. 49, pp. 8942-8948, 2010.

[21] S. Rana, S. Mallick, L. Mohapatra, G. B. B. Varadwaj, and K. M. Parida, "A facile method for synthesis of Keggin-type cesium salt of iron substituted lacunary phosphotungstate supported on MCM-41 and study of its extraordinary catalytic activity," *Catal. Today*, vol. 198, pp. 52-58, 2012.

Wimonrat Trakarnpruk was born in Bangkok, Thailand on March 7, 1956. She received her B.Sc. Chemistry degree and M.Sc. at Chulalongkorn University (Thailand) and her PhD degree at the University of Utah (USA). She has 24 years of academic experiences. She is an associate professor in Inorganic Chemistry Division, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand. Her research interests are focused on homogeneous and heterogeneous in chemical reactions: hydrogenation, hydrodesulfurization, oxidative desulfurization and oxidation .