SiO$_2$-included Cesium Polyoxotungstate Catalysts for Oxidation of Cyclohexane with H$_2$O$_2$

Wimonrat TRAKARNPRUK[1*] and Warangkana KANJINA[2]

[1]*Department of Chemistry, Faculty of Science,Chulalongkorn University, Bangkok 1033*
[2]*Program of Petrochemistry, Faculty of Science,Chulalongkorn University, Bangkok 10330*

Abstract

SiO$_2$-included cesium polyoxotungstate catalysts were synthesized by a sol-gel method and characterizied by FTIR, XRD and N$_2$ adsorption isotherms. XRD patterns prove that the cesium polyoxotungstate is uniformly dispersed in the silica network. The catalysts were used in oxidation of cyclohexane with H$_2$O$_2$. The products are cyclohexanol and cyclohexanone. The catalysts prepared by using a copolymer surfactant show higher surface area and exhibit higher activity. These catalysts are truly heterogeneous and can be reused at least 3 times.

Keywords : Polyoxotungstate, Oxidation, Cyclohexane, Hydrogen peroxide, Silica

Introduction

Selective oxidation of cyclohexane yields cyclohexanol and cyclohexanone, important intermediates in the production of adipic acid and caprolactam, in the manufacture of nylon-6 and nylon-66 polymers.[1] Polyoxometalates have been used as catalysts in oxidation of organic compounds due to the variety of their compositions, sizes, shapes, redox potentials, acidity, and solubility.[2] Most of the homogeneous oxidation of cyclohexane catalyzed by polyoxometalates was performed in acetonitrile solvent with H$_2$O$_2$ e.g. tetrabutylammonium salts of $[XW_{11}O_{39}]^{n-}$ and $[XW_{11}MO_{39}]^{(n-m)-}$ (X = P, Si, B and M^{III} = Fe, Mn),[3] $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, M = Co, Mn and Fe.[4] Co-substituted polyoxotungstate catalyst showed efficient activity in the oxidation of cyclohexane.[5] It has been reported that substitution of Cs$^+$ for H$^+$ in $Cs_xH_{3-x}PW_{12}O_{40}$ catalysts improved surface area and thermal stability compared to parent acids, the surface area is the largest when x = 2.5.[6] A problem associated with the use of these Cs salt catalysts is that the salt particles disperse as a colloid in water and organic solvents, making it difficult to separate the salt from the reaction products.[7] Therefore they were supported on a carrier.[8] The Keggin-type polyoxometalates have molecular diameter of around 1.2 nm. Heteropolytungstic acid supported on MCM-41 or amorphous silica was used as a catalyst in many organic reactions.[9,10] Our previous study in catalytic activity of the tetrabutyl-ammonium transition metal (V, Cu, Co, Fe)-substituted polyoxometalates supported on MCM-41 prepared by impregnation method for oxidation

of cyclohexane was reported.[11] Several reports in the literature have identified SiO$_2$ as a suitable support.[12] SiO$_2$-included heteropolyacids prepared by sol-gel method[13] exhibit much better catalytic activity than those prepared by impregnation method.[14] We report here the preparation of heterogeneous catalysts based on SiO$_2$-included cesium polyoxotungstate and their catalytic efficiency for the oxidation of cyclohexane with H$_2$O$_2$. A restriction of moving polyoxotungstate within solid matrix is crucial to prevent polyoxotungstate leaching into the reaction solution. H$_2$O$_2$ is a very useful oxidant because of the simplicity of handling, the environmentally friendly nature of its coproduct (water), the high oxygen atom efficiency, and the versatility.[15]

Materials and Experimental Procedures

H$_3$PW$_{12}$O$_{40}$ (Wako Pure Chemical), Cs$_2$CO$_3$ (Fluka), H$_2$O$_2$ (30 wt.% aqueous), cyclohexane (Merck), tetraethylorthosilicate (TEOS), and triblock poly (ethylene oxide)-poly (propylene oxide)-poly(ethylene oxide) copolymer or P123 (M = 5800) (Fluka) were used as received.

Catalysts synthesis and characterization

Cesium polyoxotungstate was prepared according to the literature method with slight modification.[16] by adding slowly Cs$_2$CO$_3$ 0.47 M in ethanol:H$_2$O (50:50 V/V) to H$_3$PW$_{12}$O$_{40}$ 0.47 M in ethanol. The precipitate obtained was aged overnight at 35°C, finally dried at 110°C. Its chemical

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

composition was determined by chemical analysis of W and Cs.

SiO$_2$-included cesium polyoxotungstate catalysts were prepared using two different methods:

Method A : A desired amount (10, 20 wt%) of cesium polyoxotungstate in ethanol 50 mL was added TEOS 0.1 mol (20.3 g) under stirring at room temperature. The mixture was stirred at 40°C for 1 hour and then at 80°C for 3 hours, finally dried at 110°C overnight.

Method B : Same procedure as in method A except that ethanol solution (25 ml) of P123 (14 g) was also added at room temperature. The acidity of the mixture was controlled at pH ~1 by HCl. The mixture was stirred for 5 hours. Then it was dried at 110°C overnight, resulting in clear gel. Removal of P123 was performed by calcination at 280°C for 5 hours.

The catalysts were characterized for their surface area and pore volume by the N$_2$ adsorption technique (BELSORP-mini). The X-ray powder diffraction pattern of catalysts was recorded by Rigaku, DMAX 2002/Ultima Plus diffractometer using Cu Kα radiation. Fourier-transform infrared spectra as KBr pellet were recorded on Nicolet FT-IR Impact 410 Spectrophotometer between 400-4000 cm^{-1} in transmittance mode. The amount of Cs, W was measured by dissolving the catalyst in H$_2$SO$_4$/HF (1:1 v/v) and analyzed the solution using inductively coupled plasma (ICP) on Perkin Elmer model PLASMA-1000.

Oxidation of cyclohexane

Cyclohexane, catalyst and aqueous H$_2$O$_2$ (30%) were added into a 60 ml Parr reactor. The reaction mixture was heated to 80°C and stirred for 5-15 hours. The catalyst was separated by filtration and the products were extracted with diethyl ether, dried and analyzed by GC (Shimadzu model CG-17A equipment with flame ionization detector and OV-1701 0.50 μm capillary column (30 m, 0.25 mm) using *n*-octane as internal standard. At the end of the reaction, the spent catalyst was separated, washed with water, and dried at 110°C. It was subjected to further catalytic reaction under similar condition.

Results and Discussion

The chemical formula of cesium polyoxotungstate analyzed from the ICP (Cs and W content) can be matched with Cs$_{1.7}$H$_{1.3}$PW$_{12}$O$_{40}$. Surface area and pore volume of the SiO$_2$-included cesium polyoxotungstate catalysts are shown in Table 1. The catalysts prepared by the method B show higher surface area and pore volume than those by the method A, this is due to addition of a copolymer surfactant which creates more pores in the silica matrix. Both values decreased with increasing loading of CsHPW, this could be due to deposition of cesium polyoxotungstate inside the pores or dispersion on the surface of the support.

Table 1. Characteristics of catalysts

Catalyst	%wt loading of CsHPW	Surface area m^2/g	Pore volume cm^3/g
CsHPW	-	78	0.04
SiO$_2$-included CsHPW	10	235	0.17
(method A)	20	203	0.12
SiO$_2$-included CsHPW	10	285	0.23
(method B)	20	260	0.19

The N$_2$ adsorption-desorption isotherm of the catalysts prepared by method A is shown in Figure 1. It shows Type I, according to the IUPAC classification, which is characteristic of a microporous material. A similar isotherm was obtained for the catalyst prepared by method B. The immobilization of the CsHPW in silica, by sol-gel method, creates a microporous material. The presence of micropores is confirmed by the sharp increase of the adsorbed amount of N$_2$ at a very low relative pressure. CsHPW enters into the interior of pores in the network so that the protons on the spherical surface of the CsHPW can interact with the OH groups of silanol or the bridge oxygens of Si-O-Si in the silica network.
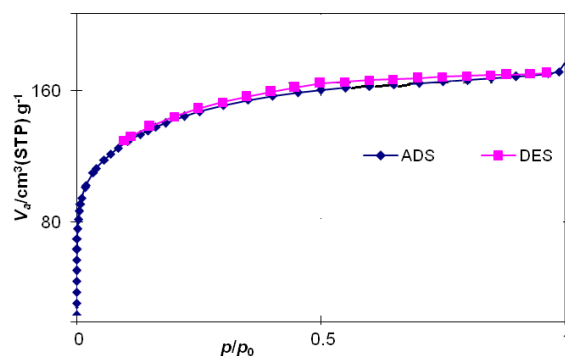

Figure 1. Adsorption-desorption isotherm of SiO$_2$-included CsHPW catalyst (method A).

Figure 2 shows the XRD patterns of the pure CsHPW and SiO$_2$-included CsHPW catalysts. It is observed that a broad band centered around $2\theta = 25°$, which is associated to the amorphous silica. No crystalline phase related to CsHPW is observed, illustrating uniform dispersion of CsHPW in the silica network in agreement with previous report.[16] It was previously reported that XRD detectable polyoxometalate crystal phase was developed on silica surface only above 20% loading. [14]
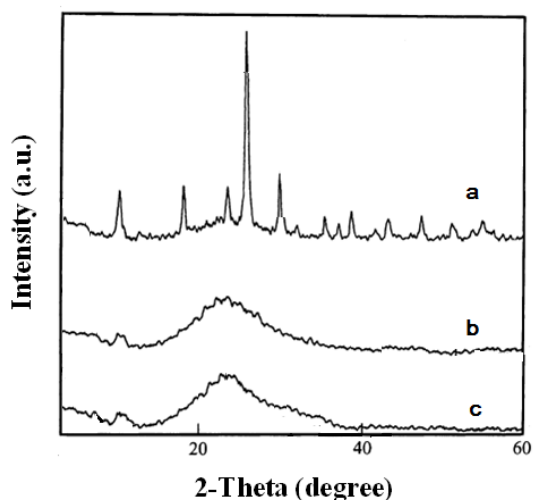

Figure 2. XRD patterns of (a) CsHPW and (b, c) SiO$_2$-included CsHPW (20 wt%) prepared by method A and B, respectively.

The characteristic IR bands of CsHPW (not shown) appear at 1077, 985, 890 and 789 cm^{-1} attribute to P-O, terminal bond (W-O), corner-sharing W-O-W and edge-sharing W-O-W, respectively. [17] FTIR spectra of the SiO$_2$-included CsHPW catalysts (10 wt% loading) are dominated by the intense and broad bands of silica, which prevent the observation of most of the CsHPW characteristic vibrational modes. However, FTIR spectrum (shown in Figure 3) of the SiO$_2$-included CsHPW catalysts (20 wt% loading) reveals a tiny band around 890 cm^{-1} in case of the catalyst prepared by method B (Figure 3b).
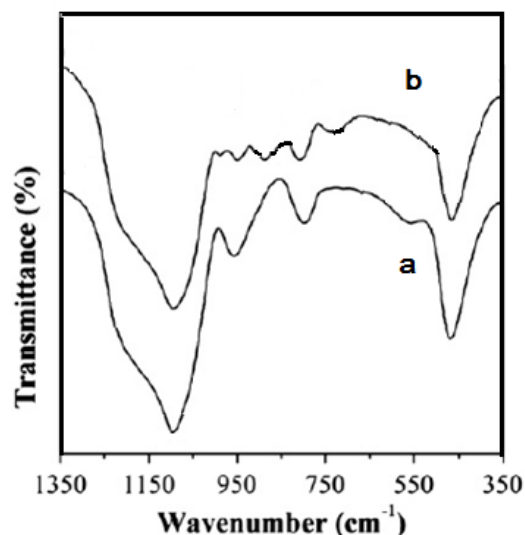

Figure 3. FTIR spectra of SiO$_2$-included CsHPW (20 wt%) prepared by (a) method A and (b) method B.

The oxidation of cyclohexane was performed using H$_2$O$_2$ as oxidant in the presence of catalyst under the same reaction conditions and the results are presented in Table 2. The oxidized products from the oxidation of cyclohexane are cyclohexanol and cyclohexanone (equation 1).
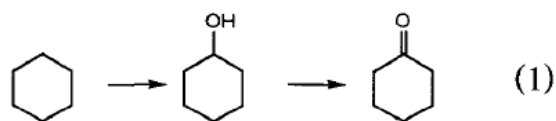

Table 2 Oxidation of cyclohexane over SiO$_2$-included CsHPW catalysts (0.4 g catalyst, cyclohexane 92 mmol, temperature 80°C)

Method	%CsHPW loading	H$_2$O$_2$/cyclohexane molar ratio	Conversion[a] (%)	Selectivity to cyclohexanone[b](%)
A	10	3	57	75
	20	3	65	75
	20	4	70	75
B	10	3	61	77
	20	3	69	78
	20	4	74	78

[a]Based on the gas chromatographic peak areas.
[b]Expressed as a percentage of the total products; cyclohexanone + cyclohexanol

The experimental results show that the catalytic activity increases with increasing CsHPW loading. The catalysts prepared by the method B show higher activity than those by the method A, this might be higher surface area and larger pore volume. With the presence of larger pores in its structure and higher surface area, this SiO$_2$-included CsHPW catalyst (method B) has more surface protons available to catalytic reaction. Higher conversion can be obtained by increasing H$_2$O$_2$/cyclohexane molar ratio from 3 to 4 while selectivity of cyclohexanone was not affected. The oxidation of cyclohexanol to cyclohexanone took place more rapidly than the oxidation of cyclohexane. For comparison, (n-C$_4$H$_9$)$_4$N)$_4$H$_3$PW$_{11}$O$_{39}$ catalyst showed low activity (35% conversion) and 60% selectivity to cyclohexanone (reaction condition : cyclohexane 18.5 mmol, catalyst 0.039 mmol, H$_2$O$_2$/cyclohexane molar ratio = 2, acetonitrile 10 ml, 80°C, 12 hours).[18] Moreover in the oxidation of cylohexanol Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ was reported to yield 90% cyclohexanol conversion at 6 h of reaction time.[17] Its high activity was explained by its high surface acid site population compared to the acidic H$_3$PW$_{12}$O$_{40}$.[19] For the supported catalyst, Cs$_x$H$_{3-x}$PMo$_{12}$O$_{40}$/SiO$_2$ showed highest activity in oxidation of benzyl alcohol when x = 1.5.[16]

Insoluble solid catalysts have practical advantages such as the easiness of separation and reusability. After the reaction, the catalyst was filtered, dried and then reused under the same reaction condition. The result shows that it can be reused 3 times without decrease in activity. However beyond that a decrease in activity (from 74% to 70% conversion) was observed, probably due to catalyst deactivation. In addition the heterogeneity of the catalytic system was confirmed by analysis of the filtrate (by ICP). No significant amount of CsHPW leached into the reaction was detected.

Conclusions

The CsHPW was successfully immobilized into silica matrix via a sol-gel method in the absence (method A) or presence of a copolymer surfactant (method B). The structural integrity of the CsHPW unit remained intact. The catalysts prepared by the method B showed higher catalytic activity for the oxidation of cyclohexane using H$_2$O$_2$ oxidant with 74% of cyclohexane conversion and 78% selectivity to cyclohexanone after 8 h of reaction at 80°C. This work demonstrates that the sol-gel method yielded good dispersion and interaction of the caesium polyoxotungstate at the silica surface.

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