Oxidation of Cyclohexane and Ethylbenzene by Hydrogen Peroxide over Co-substituted Heteropolytungstate Catalyst

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Abstract

The tetrabutylammonium salt of Co-substituted heteropolytungstate, $[(n\text{-}C_4H_9)_4N]_4 HPW_{11}Co(H_2O)O_{39}.3H_2O$ was synthesized and characterized. It was shown to be an active catalyst for the oxidation of cyclohexane and ethylbenzene. The oxidation reactions were performed using green oxidant hydrogen peroxide and acetonitrile as solvent. The major products of the oxidation of cyclohexane were cyclohexanone (K) and cyclohexanol (A). High selectivity towards K-A oil was achieved. At longer time cyclohexanol was converted to cyclohexanone. Ethylbenzene was also selectively oxidized to acetophenone. These oxidation reactions appear to be radical processes since they were totally inhibited in the presence of radical scavenger.

Key Words: Polyoxotungstate, Cyclohexane, Ethylbenzene, Oxidation, Hydrogen peroxide

Introduction

Transition metal-substituted polyoxometalates have attracted interest as catalysts in many reactions because of their thermal and chemical stability and the possibilities for modification.[1] They bear many similarities to metal complexes of macrocyclic ligands and metalloporphyrins because they possess rigid co-ordination sites surrounding a metal centre. One may visualize these compounds as having reactive low valent transition metal centers complexed by inorganic oxometalate ligands which also have a high capacity for electrons. The use of several types of polyoxometalates in homogeneous oxidative catalysis has been reviewed.[2-3] In particular, Keggin-type heteropolytungstates, $[PW_{11}O_{39}]^{n-}$ (Figure 1) were used in homogeneous oxidation with *t*-butyl hydroperoxide(Neumann & Abu-Gnim, 1989 and Matsumoto et al., 1996) and molecular oxygen. [6-7] Results using $XW_{11}Fe(H_2O)O_{39}]^{n-}$, X = P, Si and B and hydrogen peroxide were reported.[8-10] Recent reports on oxidation involved $[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$, M = Co(II), Mn(II) and Fe(III).[11] In addition, oxidation of cyclohexanone to adipic acid with air, catalysed by $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40},$ has been reported.[12]
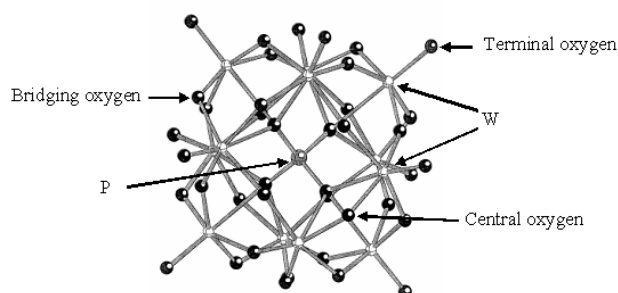
Figure 1. Structure of Keggin heteropolytungstate.

Oxidation of cyclohexane to cyclohexanol and cyclohexanone (K/A oil) is an important reaction in the industry as the two are key intermediates in the production of adipic acid (to make Nylon-66) and caprolactam (to make Nylon-6). The catalytic systems currently used in the industry for the cyclohexane oxidation employing molecular oxygen and cobalt or manganese salts limit the conversion to 5–13% (depending on the conditions) in order to achieve the required selectivity for the ketone/alcohol mixture.[13] The low conversion is due to the fact that the oxidized products are more active than cyclohexane. Therefore, they are more

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susceptible to further oxidation. Molecular oxygen is possibly the best oxidant choice. However, non-selective radical-chain reactions usually occur. Hydrogen peroxide is an interesting oxidant, due to the fact of generating environmentally benign water as by-product. It is also cheap and easy to handle.[14]

Oxidation of ethylbenzene is of importance for the production of acetophenone, which is used as a component of perfumes and as an intermediate for the manufacture of pharmaceuticals, resins and alcohols.[15] Earlier, synthesis of acetophenone was performed using stoichiometric quantities of oxidizing agents like $KMnO_4$ or $K_2Cr_2O_7$, or via Friedel–Crafts acylation reaction of aromatics by acid halide/anhydride, using stoichiometric amounts of corrosive $AlCl_3$ catalyst. The current industrial production of benzylic ketones is based on the oxidation of alkylbenzenes with molecular oxygen using cobalt acetate as the catalyst in acetic acid.[16] Zeolite encapsulated Co(II), Ni(II) and Cu(II) complexes gave acetophenone as the only partial oxidation product during ethylbenzene oxidation with H_2O_2.[17] Titanosilicates mainly catalyze ring hydroxylation of arenes with H_2O_2, whereas vanadium and chromium substituted zeolites and aluminophosphate molecular sieves have been known to favour side-chain oxidation selectively.[18]

Continuing our research on the utilization of transition metal-substituted polyoxometalates as catalyst for oxidation of sulfur compounds and cyclohexanol[19-20] we studied Co-substituted heteropolytungstate in oxidation of cyclohexane and ethylbenzene using a clean oxidant H_2O_2.

Materials and Experimental Procedures

Na_2HPO_4, $Na_2WO_4.2H_2O$, $Co(NO_3)_2.3H_2O$, tetrabutylammonium bromide (Fluka); iodine, acetonitrile (Lab-Scan); H_2O_2 (30wt% aqueous), cyclohexane, cyclohexanone, cyclohexanol, ethylbenzene, acetophenone (Merck).

Elemental analysis was performed by alkaline digestion of the catalyst followed by inductively coupled plasma emission ICP (Perkin Elmer Plasma 1000 Emission Spectrometer). FT-IR spectrum (KBr disc) was recorded on a Nicolet FT-IR Impact 410 Spectrophotometer. UV-vis was recorded using 2550 spectrophotometer Shimadzu UV probe. Hydration water content was determined by thermogravimetric analysis on a Mettler TA4000

thermobalance. Consumption of H_2O_2 was determined by titrating the remaining H_2O_2 with 0.1M $Ce(SO_4)_2$ using ferroin as indicator.[21]

Synthesis and Characterization of Catalysts

As previously described (Simões et al., 1999), $[(n\text{-}C_4H_9)_4N]_4HPW_{11}Co(H_2O)O_{39}.3H_2O$ (abbreviated $PW_{11}Co$) was synthesized as follows: Na_2HPO_4 (9.1 mmol), $Na_2WO_4.2H_2O$ (100 mmol) and $Co(NO_3)_2$ (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 and recrystallized from acetonitrile.

The formation of $PW_{11}Co$ catalyst was confirmed by UV-vis, FTIR and elemental analysis, in agreement with the literature. UV-vis λ_{max} (CH_3CN): 254, 474 nm. Anal. Found: W, 53.1; P, 0.79; Co, 1.54. Calcd.: W, 53.8; P, 0.82; Co, 1.57. Hydration water content (TGA analysis), 3. FTIR (cm^{-1}): 1063 (P-O), 965 (M=O$_{terminal}$), 887 (M-O$_{corner\ shared}$-M) and 811 (M-O$_{edge\ shared}$-M).

Oxidation Reactions with Hydrogen Peroxide

The reactions were typically carried out in a Parr reactor. Cyclohexane or ethylbenzene, catalyst and 30% H_2O_2 were mixed in 10 mL acetonitrile. The reaction was conducted at room temperature or 80°C. 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 were: for cyclohexane, initial temperature 80°C (4 minutes); temperature rate 15°C/min; final temperature 200°C (3 minutes); injector temperature 180°C and detector temperature 180°C; for ethylbenzene: initial temperature 90°C (5 minutes); temperature rate 10°C /min; final temperature 200°C (3 minutes); injector temperature 200°C and detector temperature 200°C. Quantification was done by determining the response factors of the reagents and products obtained using standard mixtures. The selectivity was calculated based on substrate (cyclohexane or ethylbenzene).

Blank reactions without catalyst and oxidant were also performed. When reactions were performed in an inert gas atmosphere, N_2 was fed into the reaction mixture before the addition of H_2O_2.

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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 conditions.

Results and Discussion

Oxidation of Cyclohexane

Cyclohexanol and cyclohexanone as main products (equation 1) were identified by FID gas chromatography by comparison with authentic standards. The trace amount of hexanoic acid was also detected by gas chromatography–mass spectrometry. The results obtained for the cyclohexane catalytic oxidation are summarized in Table 1.
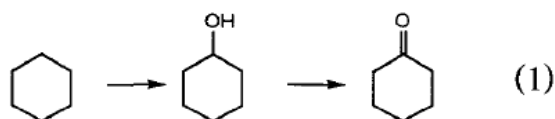
The results show that the yield was only 0.9% (entry 1) in the absence of a catalyst, and no reaction occurred without oxidant (entry 2). The temperature appears to affect the oxidation. There was almost no reaction at 30˚C (1.0% yield, entry 3), but 7% yield with 42% selectivity of cyclohexanone was obtained at 80˚C (entry 4).

At shorter time (6 hours) (entry 5), the yield and selectivity of cyclohexanone were low. This might indicate that cyclohexanol was further oxidized to cyclohexanone. We had previously reported the oxidation of cyclohexanol to cyclohexanone over this same catalyst with very high yield and selectivity.[20] The oxidation of cyclohexanol to cyclohexanone took place more rapidly than the oxidation of cyclohexane.

Higher yield (9.3%) can be obtained by increasing the H_2O_2/cyclohexane molar ratio from 2 to 4 (entry 6). When both oxidant and catalyst amounts were increased (entry 7) even higher yield

$$ (1) $$

Table 1. Oxidation of cyclohexane with hydrogen peroxide.

Entry	Catalyst	Temp. (˚C)	Time (h)	Yield[a] (%)	Selectivity[a] (%)	
					cyclohexanone	cyclohexanol
1	No catalyst	80	12	0.9	trace	trace
2	No H_2O_2	80	12	0	0	0
3	$PW_{11}Co$	30	12	1.0	trace	trace
4	$PW_{11}Co$	80	12	7.0	42	58
5	$PW_{11}Co$	80	6	3.7	33	67
6[b]	$PW_{11}Co$	80	12	9.3	42	58
7[b,c]	$PW_{11}Co$	80	12	13.0	41	59
8[b,c,d]	$PW_{11}Co$	80	12	12.9	40	60
9[e]	$PW_{11}Co$	80	12	0	0	0

Cyclohexane 2 ml (18.5 mmol), catalyst 0.04 mmol, H_2O_2/cyclohexane = 2, CH_3CN 10 ml

[a]Based on the gas chromatographic peak areas.

Yield %　　　=　　　　　$\dfrac{Area(products)}{Area(substrate + products)} \times 100$

Selectivity %　　=　　　　　$\dfrac{Yield}{Conversion} \times 100$

[b]H_2O_2/cyclohexane = 4
[c]catalyst 0.08 mmol
[d]N_2 atmosphere
[e]Experiment carried out with 18.5 mmol of 2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger.

(13.0%) can be obtained. Selectivity of cyclohexanone was 42%; it was not affected by increase in oxidant amount. Our result illustrates that selectivity of cyclohexanone is higher than that from the $[(n\text{-}C_4H_9)_4N]_6SiCoO_{39}$ catalyst using *t*-butyl hydroperoxide as oxidant.[5]

To evaluate the possible effect of air on the reaction, the experiment was conducted under a nitrogen atmosphere (entry 8). A similar result to that in air was obtained. Therefore, the possibility of auto-oxidation may be excluded.

Oxidation of cyclohexane by H_2O_2 appears to be a radical process because addition of 2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger, inhibited the formation of any product of cyclohexane oxidation (entry 9).

It should be mentioned that our result is in contrast to the Fe catalyst of which cyclohexyl hydroperoxide was the main product.[22] In that work cyclohexyl hydroperoxide was analyzed by reduction with triphenylphosphine to give cyclohexanol following Shul'pin's method[23]. It was demonstrated that cyclohexyl hydroperoxide as a primary product slowly decomposed to form cyclohexanol and cyclohexanone. In our work, we also applied this method and found no cyclohexyl hydroperoxide under the reaction conditions used. A similar result (no cyclohexyl hydroperoxide

after 12 hours reaction time) was reported on oxidation of cyclohexane over $[(n\text{-}C_4H_9)_4N]_7H_3$ $[Co_4(H_2O)_2(PW_9O_{34})_2]$.[11]

An important point to consider is the efficiency of usage of H_2O_2 oxidant in the reaction. For practical purposes the efficiency of usage of H_2O_2 in the case of cyclohexane oxidation should not be lower than 40%.[3] At lower efficiencies the cost of the oxidant may be too high for the industrial production of oxygenated derivatives of cyclohexane. In this work H_2O_2 efficiency values seem quite good, in the range of 73-76%.

The metal-catalyzed hemolytic decomposition of H_2O_2 to radicals $HO^{\bullet}$ and $HOO^{\bullet}$ can account for the formation of the 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, ketone and alcohol for oxidation of cyclohexane.[23]

Oxidation of Ethylbenzene

Oxidation of ethylbenzene yielded acetophenone and 1-phenylethanol (equation 2). The results are summarized in Table 2.
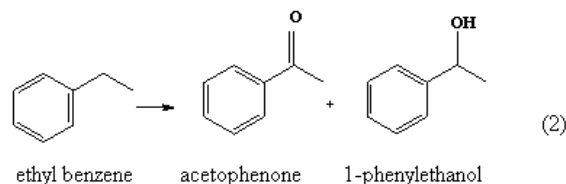

ethyl benzene   acetophenone   1-phenylethanol   (2)

Table 2. Oxidation of ethylbenzene with hydrogen peroxide.

Entry	Catalyst	Temp. (˚C)	Time (h)	Yield (%)[a]	Selectivity (%)	
					acetophenone	1-phenylethanol
1	No catalyst	80	24	0	0	0
2	No H_2O_2	80	24	0	0	0
3	$PW_{11}Co$	30	24	4.4	91	9
4	$PW_{11}Co$	80	12	17.5	88	12
5	$PW_{11}Co$	80	24	33.0	92	8
6[b]	$PW_{11}Co$	80	24	30.0	92	8
7[c]	$PW_{11}Co$	80	24	43.1	93	7
8[d]	$PW_{11}Co$	80	24	0	0	0

Ethylbenzene 0.5 g (5 mmol), catalyst 0.1 mmol, H_2O_2/ethylbenzene = 10, CH_3CN 10 ml, time 24 hours.
[a]Based on the gas chromatographic peak areas.
[b]Experiment carried out with reused catalyst after 3 times use.
[c]Catalyst 0.2 mmol
[d]Experiment carried out with 5 mmol of 2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger.

Similar results were obtained as in the case of cyclohexane oxidation. No product was found in the absence of catalyst or oxidant (entries 1, 2), respectively. In entry 3, low yield (4.4%) was obtained when the oxidation was performed at room temperature.

The effect of the reaction time on the activity can be seen in entries 4-5. At 12 hours, 17.5% yield and 88% selectivity of acetophenone were obtained. The yield was increased to 33.0% in 24 hours with an increase in acetophenone selectivity (92%). The yield and selectivity from our result are higher than that reported on Co-MCM-41 catalyst.[24]

Result on reusability of catalyst showed that it can be used 3 times with slight decrease in catalytic activity (entry 6). An attempt to increase the yield was successful by increasing the amount of the catalyst. When the catalyst amount was doubled from 0.1 to 0.2 mmol, in 24 hours yield increased to 43.1% (entry 7). As in cyclohexane oxidation, the oxidation of ethylbenzene also occurs via a radical mechanism, proved by inhibition of reaction with radical trap (entry 8).

For the reaction mechanism of ethylbenzene oxidation, hydrogen peroxide is activated by the catalyst to radicals which reacted with ethylbenzene to yield the products. 1-Phenylethanol from ethylbenzene was produced by insertion of oxygen between carbon hydrogen bond of the methylene group. Abstraction of an alcoholic OH hydrogen and the CH hydrogen by the activated hydroperoxide oxygen yielded acetophenone.

Conclusions

Co-substituted heteropolytungstate was used as tetra-n-butylammonium salt for the homogeneous oxidation of cyclohexane and ethylbenzene with hydrogen peroxide in acetonitrile. Oxidation of cyclohexane resulted in 40% selectivity of cyclohexanone under mild reaction conditions. H_2O_2 efficiency is high. The oxidation of ethylbenzene was found to give a high yield with remarkable selectivity to acetophenone (93%).

Acknowledgements

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