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Mono-substituted Keggin-polyoxometalate complexes as effective and recyclable catalyst for the oxidation of alcohols with hydrogen peroxide in biphasic system

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Abstract—Mono-substituted Keggin-polyoxymetalate complex Na_6 $[SiW_{11}ZnH_2O_{40}]{\cdot}12H_2O$ was demonstrated to be an effective catalyst for the selective oxidation of alcohols in the presence of hydrogen peroxide as oxidant. The reaction was carried out in an aqueous/oil biphasic system, which allowed easy recovery of catalyst, under relative mild conditions. The catalyst could be reused five times without appreciable loss of activity.

The selective oxidation of alcohols to carbonyl compounds, which are important precursors of various fine chemicals including drugs, vitamins, and fragrances,[1–3] is a key transformation in fine chemical industry. Because of the advantageous properties of hydrogen peroxide,[4] a number of useful procedures have been developed for H_2O_2-mediated oxidation of alcohols catalyzed by tungsten systems, such as tungstic acid, quaternary ammonium tetrakis(diperoxotungsto)phosphates, sodium tungstate + $[(n\text{-}C_4H_9)_4N]Cl$, and sodium tungstate + quaternaryammoniumhydrogen sulfate.[5] These types of reactions with the catalysts dissolved in the organic phase inherently require separation of the catalyst from the product, invariably a chromatographic procedure, for recovery of the catalyst.

In order to overcome this drawback, an alternative approach has been developed using a biphasic system, with two immiscible liquid phases, such that the homogeneous catalyst is soluble in one phase (e.g., water) and the products in the other phase (organic). The oxidation product can then be obtained by a simple phase separation. For the construction of such biphasic system, the use of water-soluble catalyst was often involved. Initially, a water-soluble palladium–phenanthroline complex has been used to catalyze the title reaction using the biphasic system.[6] However, the system still suffers from the use of both an expensive and a noble metal. Moreover, the preparation of water-soluble organic ligand was also a hard task.

Transition metal polyoxometalates have proved to be effective catalysts for the oxidation of hydrocarbons with hydrogen peroxide or molecular oxygen over the past decade.[7] In particular, transition metal mono-substituted Keggin-type heteropolyacids, $[XW_{11}MO_{39}]^{(n-m)-}$ (X = P, Si, B), in which a transition metal cation, M^{m+}, is coordinated to the binding sites of lacunary heteropolyanions $[XW_{11}O_{39}]^{n-}$, have generated substantial interest as oxidative catalysts. This is because their thermal and chemical stability and redoxic and acidic properties could be controlled at the atomic/molecular levels by changing the constituent elements (other transition or main group metals) without affecting the Keggin-type primary structure.[8] Previously, Ronny Neumann's group demonstrated feasibility for the application of water-soluble polyoxometalates, Na_{12-} $[WZnZn_2(H_2O)_2\text{-}(ZnW_9O_{34})_2]$, in the biphasic oxidation of alcohols and

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contributed more than 10 papers in this area.[9] To expand the applications of water-soluble polyoxometalates in the biphasic oxidation of alcohols, now, we reported the oxidation of alcohols with aqueous hydrogen peroxide using a mono-substituted Keggin-polyoxometalate, Na_6 $[SiW_{11}ZnH_2O_{40}]{\cdot}12H_2O$, as catalyst in biphasic system without the use of organic solvent. Compared with conventional catalytic systems, this methodology offers significant improvements with regard to catalytic efficiency, simplicity in operation, cost efficiency, and green aspects avoiding toxic catalysts and solvents.[10]

The catalyst was prepared by the following procedure: 28 g (0.009 mol) $H_4SiW_{12}O_{40}{\cdot}7H_2O$ and 100 ml water were mixed and heated to 95 °C; 7.2 g $NaHCO_3$ (0.085 mol) was then added to the aqueous solution, adjusting the pH value to 6; subsequently, 10 ml hot $ZnNO_3{\cdot}6H_2O$ (3.1 g, 0.013 mol $ZnNO_3{\cdot}6H_2O$) solution was added carefully. After 10 min of stirring at 95 °C, the solution was quickly filtered. The filtrate was dried at 95 °C for 2 h, and a white powder was obtained. The structure of the powder was confirmed as Na_6 $[SiW_{11}ZnH_2O_{40}]{\cdot}12H_2O$ (abbreviated as $SiW_{11}Zn$) from IR, UV spectroscopic data, and elemental analysis. Other catalysts were synthesized according to the standard method.[11]

Initially, oxidation of cyclohexanol was used as the model reaction to test the activities of various catalysts $[SiW_{11}MO_{39}]^{(n-m)-}$ (M = Zn, Cu, Ni, Co, Fe, Mn, Cr, V) and the results are listed in Table 1.[12] It was observed that $SiW_{11}Zn$ was the best catalyst for the reaction, and cyclohexanol was completely consumed after 7 h reaction with exclusive selectivity to cyclohexanone. Other M-containing catalysts are also capable of catalyzing the model reaction, but their efficiencies seem to be slightly inferior as compared with that of $SiW_{11}Zn$. It should be pointed out here, besides the unreacted cyclohexanol, the only product was cyclohexanone by the analysis of GC–MS, indicating the specific character of our catalysts for the oxidation of cyclohexanol. When SiW_{12}, the transition metal was omitted, was used as a catalyst, only unreacted cyclohexanol was detected. These results indicated that the transition metal in catalysts might play a pivotal role in the present oxidation reaction.

Table 1. Oxidation of cyclohexanol with hydrogen peroxide over various polyoxometalate catalysts at 363 K[a]

Catalyst	Conversion of cyclohexanol (%)	Selectivity of cyclohexanone (%)
SiW_{12}	0	0
$SiW_{11}V^{(IV)}$	70	100
$SiW_{11}Cr^{(VI)}$	69	94.3
$SiW_{11}Mn^{(IV)}$	70.4	97.7
$SiW_{11}Fe^{(III)}$	52.9	∼100
$SiW_{11}Co^{(II)}$	43.8	100
$SiW_{11}Ni^{(II)}$	52.8	100
$SiW_{11}Cu^{(II)}$	38.6	100
$SiW_{11}Zn^{(II)}$	100	100

[a] Reaction condition: cyclohexanol/30% H_2O_2/catalysts = 670:1005:1, temperature: 363 K, reaction time: 7 h, 10 ml water.

Having the best catalyst in hand, various alcohols, including primary and secondary alcohols, were submitted to the condition of Table 1 and the results are listed in Table 2. Secondary alcohols, such as 2-pentanol, 2-hexanol, and cyclooctanol, were converted to the corresponding ketones with H_2O_2 using $SiW_{11}Zn$ as catalyst in a short period with excellent conversions and good selectivity. Indeed, secondary allylic alcohols, such as 2-clycohexen-1-ol, 1-octen-3-ol could also be oxidized effectively to the corresponding α,β-unsaturated ketones. Primary alcohols, for instance, ethanol, 1-pentanol, benzyl alcohol, are all worked well under our conditions, but the formation of the corresponding carboxylic acids was proved to be the predominant reaction, and only slight amount of corresponding aldehydes was detected after the reaction. It is worth noting that 1,3-diol, 2-ethylhexane-1,3-diol underwent the same oxidation reaction under our conditions to give high selectivity of the partial oxidation product, 2-ethyl-1-hydroxy-3-hexanone, which implies that primary alcohols were more difficult to oxidize than secondary alcohols over $SiW_{11}Zn$ catalyst. It is well known that benzyl alcohol has higher reactivity as compared with that of linear aliphatic primary and secondary alcohols. On the one hand, benzyl alcohol could be completely converted to benzoic acid even at room temperature within 2 h. On the other hand, our experimental results also show that $SiW_{11}Zn$ catalytic system does not induce the unproductive decomposition of H_2O_2 to any great extent and enables the economic use of the oxidant, namely, molar ratio of H_2O_2 to cyclohexanol is 1.5:1. With a higher molar ratio, the product selectivity is decreased to some extent; for the alcohols with relatively poor reactivity, for example, 2-octanol, a 5-fold molar excess of H_2O_2 was required.

One of the main aims of using mono-substituted Keggin-polyoxometalate complexes as catalysts was to study the possibility of its recycle and reuse. We found that the catalyst, $SiW_{11}Zn$, could be easily recycled by a simple procedure. For example, in the oxidation of cyclohexanol, the product, cyclohexanone, could be decanted from the biphasic system. To prevent the accumulation of water in the reused experiments, the recovered aqueous solution could be heated to 90 °C for 0.5 h under vacuum (12 mmHg) before each run. The remaining $SiW_{11}Zn$ aqueous residue was therefore recharged with cyclohexanol and hydrogen peroxide as above. Reaction workup was carried out again. We found that the reaction was carried out five times in consecutive run with only a slight decrease in activity (Table 2). Table 2 also lists ToN of catalyst for different alcohol oxidation reactions. Compared with Neumann's catalyst, the $SiW_{11}Zn$ is more effective for various alcohol oxidation reactions.

Figure 1 shows IR of the fresh, recycled and $SiW_{11}Zn$ treated with 30% H_2O_2. The IR spectrum of fresh $SiW_{11}Zn$ shows six peaks at 1016, 975, 921, 884, 793, and 532 cm^{-1}, indicating that the $SiW_{11}Zn$ is a Keggin-type structure polyoxometalates.[8b,13] There is not an obvious difference between the IR spectra of the recycled and fresh samples. After addition of hydrogen peroxide, a new peak at 623 cm^{-1} was observed. It is

Table 2. Selective oxidation of alcohol with aqueous hydrogen peroxide by $SiW_{11}Zn$[a]

Substrates	Eff. conv. of H_2O_2 (%)	Alcohols conv. (%)	Product selectivity (%)		TON
Benzyl alcohol[b]	99	100		Benzoic acid (100)	544(250[i])
4-bromo-benzyl alcohol[b]	99	100		4-Bromo-benzoic acid (100)	366
4-Nitrobenzyl alcohol[b]	99	100		4-Nitrobenzoic acid (100)	417
1-Phenyethanol[c]	99	100	Acetophenone (100)		471(250[i])
Ethanol	91	77	Acetaldehyde (7)	Acetic acid (93)	942
1-Pentanol	89	58	Pentanal (8)	Pentanaonic acid (92)	340(165[i])
Propan-2-ol	99	96	Acetone (95)		830(233[i])
2-Butanol	99	98	2-Butanone (100)		
2-Pentanol	99	100	2-Pentanone (100)		577(235[i])
2-Hexanol	99	100	2-Hexanone (100)		697
2-Octanol	86	91	2-Octanone (100)		356(228[i])
2-Ethyl-1,3-hexanediol	99	100	2-Ethyl-1-hydroxy-3-hexanone (93)	Butanoic acid (7)	398(250[i])
2,2,4-Trimethyl-1,3-pentanediol	99	100	2,2,4-Trimethyl-1-hydroxy 3-pentanone (97)		385
Cyclohexanol	99	100	Cyclohexanone (100)		600(250[i])
	96	98[d]			
Cyclooctanol	99	100[e]	Cyclooctanone (100)		479
	76	95[f]			(238[i])
	85	78[g]			195
	93	93[h]			233
2-Cyclohexen-1-ol	99	100	2-Cyclohexen-1-one (100)		638
1-Octen-3-ol	99	100	1-Octen-3-one (100)		488
Menthol	99	99	Menthone (100)		401
Borneol	99	100	Camphor (100)		406

[a] Reaction condition: 2 ml substrates; 0.1 g of catalyst; 4 ml H_2O_2(30%); temperature 363 K; reaction time: 9 h; 10 ml water.

[b] 2 ml substrates; 0.1 g of catalyst; 2 ml H_2O_2(30%); reaction time: 2 h.

[c] 2 ml substrates; 0.1 g of catalyst; 3 ml H_2O_2(30%); reaction time: 7 h.

[d] The fifth run.

[e] $SiW_{11}Zn$ as catalyst.

[f] Na_{12-} $[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$ as catalyst.

[g] $Q_3PW_{12}O_{40}$ as catalyst (Q = cetylpyridinium).

[h] $Q_3[PO_4(W(O)(O_2)_2)_4]$ as catalyst. The remaining H_2O_2 after reaction was estimated by titration with KI solution.

[i] Calculated from Ref. 9d.

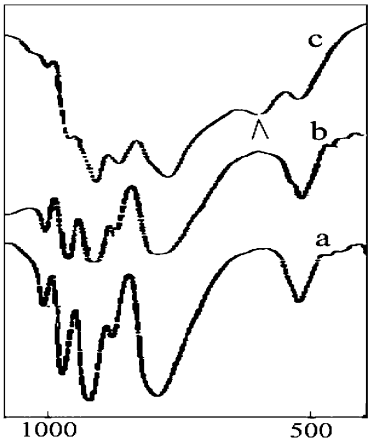

Figure 1. IR spectra of $SiW_{11}Zn$ before during and after reaction: (a) fresh $SiW_{11}Zn$; (b) used $SiW_{11}Zn$; (c) $SiW_{11}Zn$ in 30% H_2O_2.

most likely attributed to the formation of a peroxometal species.[14] After decomposition of the excess hydrogen peroxide with aqueous KI, the IR spectrum is almost identical to that of fresh $SiW_{11}Zn$. The results of IR characterization indicated that the $SiW_{11}Zn$ is a stable catalyst in the reaction system.[8] But at this research stage, the exact structure of the peroxometal species and the activating site are not clear. However, several possible structures for the active peroxometal species could be deduced as shown in Figure 2 according to the previous analogy research.[15]

As to the reaction mechanism, based on the hypothesis about the structures of peroxometal species mentioned above, it could yet be deduced as shown in Figure 3: at the beginning of the reaction, $SiW_{11}Zn$ catalyst reacted with 30% H_2O_2 to produce species, which may be the active intermediate for the oxidation of alcohol, then peroxometal species reacted with alcohol to afford the corresponding product.

In summary, we have described an efficient catalytic oxidation procedure of alcohols with hydrogen peroxide using mono-substituted Keggin-polyoxometalate complexes as catalysts. Many primary and secondary alcohols could be converted to the corresponding ketones and carboxylic acids with good to excellent conversion and selectivity. This biphasic system based on $SiW_{11}Zn$ permits extensive recycling of the catalyst without significant loss in activity. IR investigation revealed that peroxometal might be the active species for the oxidation of alcohol.

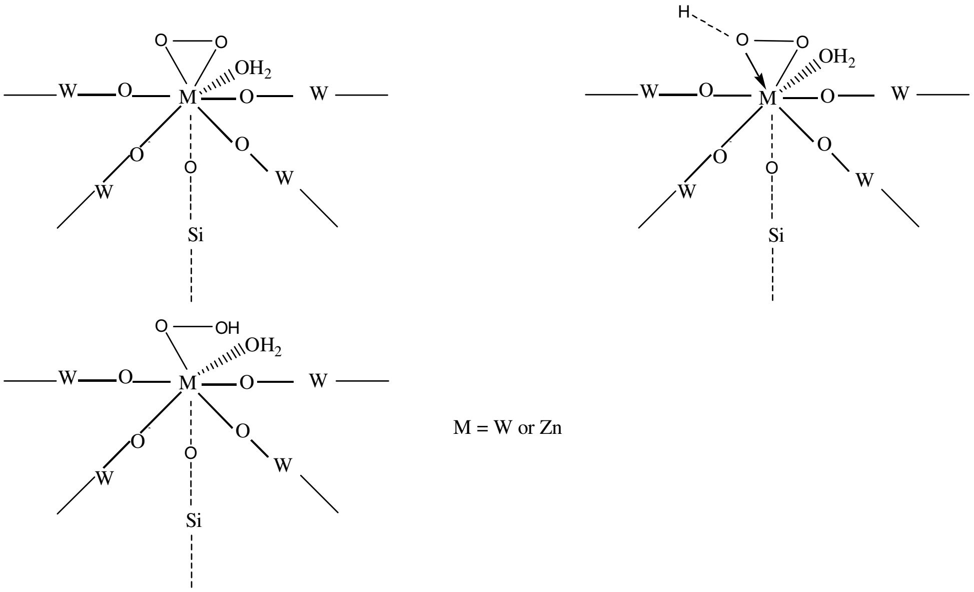

Figure 2. Possible structure of the peroxometal species.

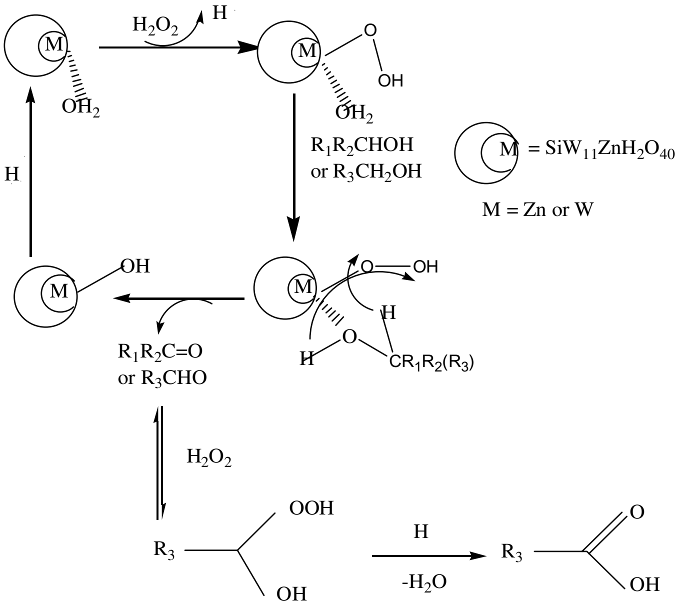

Figure 3. Possible mechanism for oxidation of alcohols.

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12. Typical oxidation procedure is as follows: 0.1 g catalyst, 10 ml water, and 0.02 mol (2 ml) alcohol were added into a 25 ml round-bottomed flask equipped with a magnetic stirring bar and reflux condenser. The mixture was stirred at desired temperature for 30 min, and then 0.04 mol (4 ml) aqueous hydrogen peroxide (30%) was added. The biphasic mixture was stirred at 90 °C for 9 h. At the end of the reaction, the reaction mixture was cooled to room temperature, and 10 ml of di-*n*-butyl ether was added. Then, the organic phase was separated and analyzed by gas chromatograph (PE Autosystem XL), using chlorobenzene as internal standard, with a flame ionization detector and a 30 m SE-54 capillary column or GC–MS (Agilent6890N/5973N).
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