

Selective oxidation of sulfide catalyzed by peroxotungstate immobilized on ionic liquid-modified silica with aqueous hydrogen peroxide

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Abstract

Two kinds of catalysts of peroxotungstates immobilized on ionic liquid-modified silica have been synthesized and characterized. By comparing with other heterogeneous catalysts, the most characteristic of these heterogeneous catalysts is the catalyst formed from the combination of catalytic active center peroxotungstate with an ionic liquid. Thereinto, ionic liquid-modified supported catalysts provide the hydrophobic environment for organic reactions. We presume that the heterogeneous catalyst would display excellent catalytic ability depending on the additive effect of an ionic liquid and peroxotungstate. Their catalytic properties in oxidation of sulfides to sulfoxides and sulfones were investigated with 30% aqueous hydrogen peroxide at room temperature. These recoverable catalysts both exhibit high catalytic activities in the oxidation reaction of sulfoxides and provide excellent chemselectivities towards sulfur groups with unsaturated double bonds when the aqueous hydrogen peroxide was greatly in excess. The yields of methyl phenyl sulfoxide were still satisfied when the catalyst was reused for a sixth time.

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Keywords: Peroxotungstate; Hydrogen peroxide; Ionic liquid-modified silica

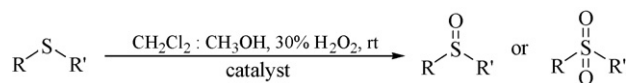
1. Introduction

There is an increasing requirement for selective and efficient methods for the preparation of sulfoxides and sulfones due to their importance as synthetic intermediates for C–C bond formation, molecular rearrangement, functional groups and their requirement in a variety of pharmaceuticals [1–3]. The oxidation of sulfide is a straightforward technique to obtain sulfoxides and sulfones. The traditional oxidants used include organic peracids, transition metal oxides and inorganic oxides [4–8]. However, these oxidants are disadvantaged in that they produce equimolar amounts of deoxygenated waste, which in the reaction system not only makes the isolation of the product difficult, but also brings about a negative effect on the environment when discharging this waste. In this age of awareness of green chemistry, clean production and atomic economy, the replacement of traditional oxidants by green oxidants such as oxygen, ozone, immobilized oxide, and hydrogen peroxide, has become a key step to realize the environmental benign technique. Hereinto, hydrogen

peroxide as oxidant has attracted increasing attention owing to the formation of harmless by-products and the simplified operation after reaction. However, aqueous hydrogen peroxide is a moderate inorganic oxidant. Accordingly, the chief problem to realize the oxidation reaction with aqueous hydrogen peroxide is establishing highly selective and efficient catalytic systems.

Previous research has adequately proved that peroxotungstate complexes are effective catalysts to activate hydrogen peroxide in the oxidation reaction [9–15], and there are some reports about the use of the homogenous peroxotungstate in the oxidation of sulfides [12,16,17]. Although the homogenous peroxotungstates display favorable catalytic abilities, the heterogeneous catalysts are of significant industrial interest since they can be easily separated from the reaction mixture and recycled. Some heterogeneous catalysts have been applied to the oxidation of sulfides [18–22]. However, these catalytic systems suffer from at least one of the following disadvantages, such as long reaction time, low conversion of sulfide, bad selectivity of sulfoxide and sulfone, high catalyst amount and excessive H₂O₂. Here, we have developed a supported peroxotungstate to oxidize sulfides under mild conditions with aqueous hydrogen peroxide. By comparing with other heterogeneous catalysts, the most characteristic of these heterogeneous catalysts is the catalyst

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Scheme 1.

formed from the combination of peroxotungstate with an ionic liquid, which has received much attention in recent years as a potentially environmentally benign catalyst or as a suitable reaction media for organic reactions [23–27]. We presume that the heterogeneous catalyst would display excellent catalytic ability depending on the additive effect of peroxotungstate and an ionic liquid, which provides the hydrophobic environment for organic reactions. The catalytic properties of peroxotungstate immobilized on ionic liquid-modified silica were examined for the oxidation of sulfides to sulfoxides and sulfones under mild condition (Scheme 1).

2. Experimental

2.1. Materials and apparatus

Allyl methyl sulfide, butyl sulfide, allyl sulfide, ethyl methyl sulfide, thioanisole, methyl(4-nitrophenyl) sulfide, diphenyl sulfide and potassium molybdate dihydrate were used as purchased. A 30% hydrogen peroxide was of A.R. grade and was titrated by a standard KMnO_4 solution, which was standardized with primary standard grade $\text{Na}_2\text{C}_2\text{O}_4$ before use. The organic solvent needed was pretreated according to standard method.

The SEM–EDAX was performed on a Philips-FEI Quanta200 scanning electron microscopy equipped with an EDAX energy dispersive X-ray analysis. The BET surface areas of the materials were measured by nitrogen adsorption Peking Pioneer-2002 ST-03A. C, H and N element analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded separately on a Bruker Equinox-55 spectrophotometer (KBr pellets in the range $400\text{--}4000\text{ cm}^{-1}$). GC analysis was performed on an Agilent 6890N(G1540N) using a capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) with a FIT detector ($250\text{ }^\circ\text{C}$), nitrogen as the carrier gas. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE300 MHz spectrometer (CDCl_3 as solvent, TMS as an internal standard).

2.2. Synthesis of catalysts

2.2.1. Preparation of $\text{SiO}_2\text{-I}$

Before silylation of SiO_2 surface, the carrier was activated as following procedure: Mesoporous silica gel was stirred with concentrated hydrochloric acid at room temperature for 4 h and then refluxed for 10 h. The resulting mixture was filtered, washed thoroughly with the deionized water and acetone. The carrier was dried under vacuum at $140\text{ }^\circ\text{C}$ prior to undergoing chemical surface modification. The BET surface area of silica precursor was $361\text{ m}^2\text{ g}^{-1}$ with 5.65 silanol groups per nm^2 dispersed on the surface of pretreated SiO_2 . The aim of pretreatment is to enhance the content of silanol groups and to eliminate metal oxide and nitrogenous impurity.

$\text{SiO}_2\text{-I}$ was prepared according to the previous procedures [28]. Five grams of activated silica precursor were refluxed with 18 mmol of γ -chloropropyltriethoxysilane in 50 ml anhydrous toluene protected by N_2 for 24 h. The superfluous γ -chloropropyltriethoxysilane was removed by soxhlet extraction using a mixed solvent of 1/1 diethyl ether and dichloromethane.

2.2.2. Preparation of ionic liquid-modified silica $\text{SiO}_2\text{-2-Im}$

Functionalisation of $\text{SiO}_2\text{-I}$ with *N*-methylimidazole was vigorously stirred in anhydrous MeCN under refluxed condition for 24 h. After filtering the resulting materials were washed by soxhlet extraction with acetone as solvent. The ionic liquid-modified silica $\text{SiO}_2\text{-2-Im}$ was obtained by the direct reaction of the above precursor and KPF_6 in CH_3CN at room temperature for 48 h. After the reaction, the obtained material was washed consecutively with water and acetone, then, dried under vacuum at $70\text{ }^\circ\text{C}$ over night.

2.2.3. Preparation of supported peroxotungstate immobilized on ionic liquid-modified silica $\text{SiO}_2\text{-W}_2\text{-Im}$

Five millilitres 30% H_2O_2 was added to the solution of $\text{K}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.724 g, 2 mmol) in 5 ml water while being stirred at room temperature [29,30], the resulting yellow solution was treated with dilute hydrochloric acid until it just turned colorless. One gram of the $\text{SiO}_2\text{-2-Im}$ was added to this colorless solution and the suspension was stirred at room temperature for 24 h. During the reaction, binuclear peroxotungstate anion was exchanged on the ionic liquid-modified silica $\text{SiO}_2\text{-2-Im}$. After filtration and dry, the $\text{SiO}_2\text{-W}_2\text{-Im}$ was obtained [31].

The preparation of $\text{SiO}_2\text{-W}_2\text{-Py}$ is similar to that of $\text{SiO}_2\text{-W}_2\text{-Im}$.

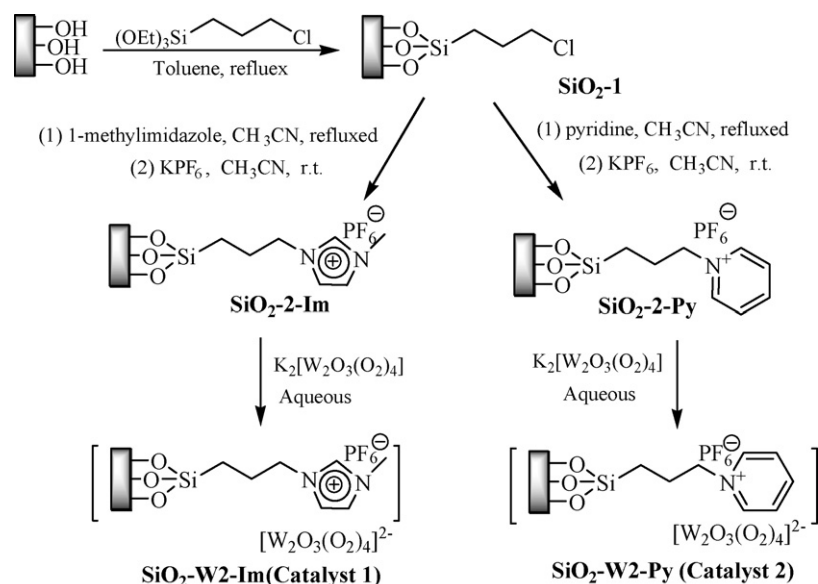
2.3. General procedure of catalytic oxidation experiments

2.3.1. A typical procedure for the selective oxidation of sulfides to sulfoxides

To a 25 mL flask with a mixed solvent of $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1:1 molar ratio), the catalyst (1.5 mol.% with respect to substrate), sulfide (1 mmol) and 30% aqueous hydrogen peroxide (1.1 mmol) were added successively. The resulting mixture was stirred electromagnetically at room temperature. The conversion of substrates and yield of sulfoxides were periodically determined by GC analysis during the oxidation. The content of each component was calculated by the method of area \times calibration factor. The products were confirmed by ^1H NMR and ^{13}C NMR. After the completion of the reaction, the catalyst was separated by the filtration, washed with the ethanol, and dried in vacuo before being recycled. The filtrates of crude sulfoxides were chromatographed on silica gel to afford the corresponding pure compounds for determination.

2.3.2. A typical procedure for the selective oxidation of sulfides to sulfones

The methods of oxidizing sulfides to sulfones are similar to that of sulfoxides except that the ratio of catalyst, H_2O_2 ,



Scheme 2.

and sulfide was changed from 1.5:110:100 to 2:250:100. The conversion of substrates and yield of sulfones were periodically determined by GC analysis during the oxidation. The content of each component was calculated by the method of area \times calibration factor. The products were confirmed by ^1H NMR and ^{13}C NMR.

3. The results and discussion

3.1. Catalysts preparation

The heterogeneous catalysts were synthesized by grafting an ionic liquid onto the modified mesoporous inorganic materials by ion exchange, and then anchoring the catalytic active center peroxotungstate onto the immobilized ionic liquid (Scheme 2). The results of elemental analysis, IR spectra and SEM–EDAX studies of the catalysts displayed that the ionic liquid anion PF_6^- was not exchanged completely by the binuclear peroxotungstate anion. Thereby, the trait of the homogeneous reaction of the ionic liquid was transferred to the heterogeneous catalyst. Simultaneously, the grafted ionic liquid avoids the disadvantage that a little loss in the homogeneous system would lead to an increase in cost.

3.2. Characterization of the intermediates and catalysts

The elemental analysis, BET surface areas and Metal anion loading of intermediates and catalysts were listed in Table 1. Elemental analysis revealed that 0.59 mmol and 0.61 mmol of ionic liquid fragments per gram grafted on the $\text{SiO}_2\text{-2-Im}$ and $\text{SiO}_2\text{-2-Py}$ respectively. The loading amounts of binuclear anion $[\text{M}_2\text{O}_3(\text{O})_4]^{2-}$ were 0.22 and 0.23 mmol/g for $\text{SiO}_2\text{-2-Im}$ and $\text{SiO}_2\text{-2-Py}$ respectively, which was calculated by the SEM–EDAX spectra. Compared with the parent SiO_2 , the BET surface areas of catalysts significantly decreased from 361 to 199 and 185 m^2g^{-1} .

3.3. IR spectral study

The IR spectral data of intermediates and supported catalysts are listed in Table 2. Disappearance of the (C–Cl) band on the $\text{SiO}_2\text{-2}$ suggests the formation of ammonium. The strong stretching vibrations appearing near 830 cm^{-1} showed the bands characteristic of (P–F), but its vibration weakens greatly in the catalysts. The IR spectrums of supported catalysts are similar to those of previously reported peroxotungstate derivatives [32]. The stretching vibrations near the 950 cm^{-1} was assigned to the presence of $\text{M}=\text{O}$ for catalysts. The presences of strong bands

Table 1
Analytical data of intermediates and catalysts

Compound	Elemental analyses (%)			BET SA (m^2g^{-1})	Metal anion loading (mmol/g)
	C	H	N		
$\text{SiO}_2\text{-1}$	6.46	1.09		325	
$\text{SiO}_2\text{-2-Im}$	6.03	0.89	1.65	300	
$\text{SiO}_2\text{-2-Py}$	6.27	0.76	0.86	259	
Catalyst 1	5.08	0.74	1.35	199	0.22
Catalyst 2	5.23	0.60	0.74	185	0.23

Table 2
IR spectral data for intermediates and catalysts [band maxima (cm⁻¹)]

Complex	$\nu(\text{C-H})$	$\nu(\text{C=N})$	$\nu(\text{M=O})$	$\nu(\text{O-O})$	$\nu[\text{M}(\text{O}_2)]$	$\nu(\text{M}_2\text{O})$	$\nu(\text{P-F})$
SiO ₂ -1	2917, 2848	689(C-Cl)					
SiO ₂ -2-Im	2924, 2844	1628					836
SiO ₂ -2-Py	2922, 2852	1640					834
Catalyst 1	2921, 2848	1634	964	878	613, 541	705, 473	832
Catalyst 2	2924, 2844	1628	945	882	588, 536	702, 476	830

around 870 cm⁻¹ in the spectra are attributable to stretching vibrations of peroxy group O–O. These data are near the vibration of O–O in hydrogen peroxide at 877 cm⁻¹ [33]. The most characteristic frequency in the stretching vibrations of catalysts appearing between 530 and 620 cm⁻¹ are attributed to the existence of $\nu_{\text{sym}}[\text{M}(\text{O}_2)]$ and $\nu_{\text{asym}}[\text{M}(\text{O}_2)]$ [33]. The above stretching vibrations strongly suggest the presence of O–O in the catalysts. The stretching vibrations of $\nu_{\text{asym}}(\text{M}_2\text{O})$ and $\nu_{\text{sym}}(\text{M}_2\text{O})$ could be observed near 700 and 450 cm⁻¹, respectively.

3.4. Catalytic abilities of catalysts

3.4.1. Oxidation of sulfides to sulfoxides

The synthesized catalysts were used in the oxidation of various sulfides with aqueous H₂O₂ in the mixed solvent of MeOH and CH₂Cl₂ (Table 3). The data in Table 3 showed that sulfoxides could be obtained in high yields in the presence of two catalysts with trace over-oxidation product when the mixture of catalyst, H₂O₂, and sulfide (in a molar ratio of 1.5:110:100) were stirred vigorously in air and at room temperature for 2.5–4 h. Compared

with previous reports about using ordinary silica-based tungstate catalyst [31], the amount of H₂O₂ needed in the catalytic oxidation system was reduced greatly from 3 times to 1.1 times (based on the amount of sulfide).

Control experiments indicate that in the absence of the catalyst, the oxidation of thioanisole at the same condition gives methyl phenyl sulfoxide in a rather low yield of 18.3%. It was found that both aromatic and aliphatic sulfides could be used. The yields of saturated aliphatic sulfides are higher than those of sulfides with unsaturated functional groups. Moreover, these two catalysts provide excellent chemoselectivity towards the sulfur group of the substituted sulfides containing other functional groups susceptible to oxidation. As an example, allyl methyl sulfoxide and allyl sulfoxide were obtained in high yield without epoxidation products. Interestingly, the reaction does not appear to be affected significantly by steric effects as the yields are comparable with those of methyl phenyl sulfoxide and diphenyl sulfoxide. At the same time, even the presence of a strong electron withdrawing group NO₂ in the phenyl ring of diaryl sulfides does not affect the sulfoxide yield.

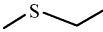
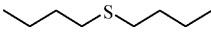

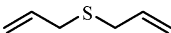
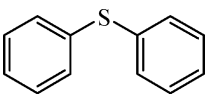
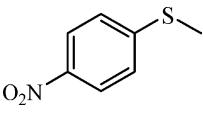
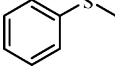
Table 3
Oxidation of sulfides to sulfoxides using 30% H₂O₂ catalyzed by supported peroxotungstate^a

Entry	Sulfide	Temperature (°C)	Time (h)	Catalyst 1		Catalyst 2		
				Conv. (%)	Yield (%) ^b	Conv. (%)	Yield (%) ^b	
1		10	3	100	94.8	100	94.7	
2		14	2.5	100	87.9	100	89.1	
3		9	4	89.6	85.1	94.3	89.4	
4		12	5	90.1	82.6	91.9	80.4	
5		12	5	93.2	88.1	95.3	84.8	
6		1st	8	2.5	97.9	91.9	95.6	90.1
		2nd	8	2.5	91.4	86.6		
		3rd	8	2.5	98.5	90.7		
		4th	8	2.5	96.8	89.7		
		5th	10	2.5	99.2	89.3		
		6th	10	2.5	96.2	90.7		

^a Reaction conditions—1.5 mol.% of catalyst, 1.1 equiv. of H₂O₂, were stirred for 2.5–4 h at room temperature.

^b GC yields.

Table 4
Oxidation of sulfides to sulfones using 30% H₂O₂ catalyzed by supported peroxotungstate^a

Entry	Sulfide	Temperature (°C)	Time (h)	Catalyst 1 yield (%) ^b	Catalyst 2 yield (%) ^b
1		10	4	99.3	98.7
2		14	7	90.2	87.8
3		14	6	86.1	79.6
4		14	5	92.2	80.7
5		12	7	82.3	84.4
6		13	7	78.9	80.3
7		10	5	96.3	90.4

^a Reaction conditions—2 mol.% of catalyst, 2.5 equiv of H₂O₂, were stirred for 4–7 h at room temperature.

^b GC yields.

It is recommended that the molar ratio of the catalyst and sulfide is 1.5:100. When the amount of catalyst was reduced to 1 mol.% in the oxidation of thioanisole, not only the reaction velocity slows down, but also the yield of sulfoxide is greatly cut down. Even the reaction time was prolonged to 3.5 h; the yield is only 87.3%. Likewise, an unsatisfied yield of sulfoxide was obtained using 2 mol.% catalyst. The reason exists in the appearance of the overoxidation product. Moreover, the optimum molar ratio of sulfide and H₂O₂ is 1:1.1. Although the conversion of the sulfide improved with the increasing amount of the H₂O₂, the yield of the sulfoxide decreased due to that the fall in selectivity of the sulfoxide.

It is worthy to note that when the binuclear peroxo anion [M₂O₃(O)₄]²⁻ was replaced with the mononuclear anion WO₄²⁻, the yield of methyl phenyl sulfoxide was reduced from the highest yield of 91.9% to 44.0% and 24.4% for the imidazole cation and pyridine cation, respectively, under the same reaction condition. Even when the reaction was carried out in a molar ratio of 2:150:100 of catalyst, H₂O₂, and sulfide, the highest yield is only 55.7%. This result is in accordance with the previous research that compared with their mononuclear analogues [34], the dinuclear peroxotungsten species provide good catalytic properties for oxidation owing to the former having more active oxidizing moieties than the latter.

3.4.2. Recycle ability of the catalyst

In order to investigate the recyclability of the heterogeneous catalyst, we selected thioanisole as a model substrate due to its relative unreactive sulfoxide, and chose catalyst 1 to reuse. The results of the recycling experiments indicated that the yields of the methyl phenyl sulfoxides were consistently high after six uses (Table 3), which illuminated the fact that the catalytic activity of the catalyst did not change significantly, as compared with fresh catalyst. The SEM–EDAX spectra analysis performed on the recovered catalyst after six uses showed that

the catalytic center content of tungstate decreased slightly after reuse.

3.4.3. Oxidation of sulfides to sulfones

When the molar ratio of catalyst, H₂O₂, and sulfide was changed from 1.5:110:100 to 2:250:100, oxidation of the sulfides obtained the corresponding sulfones at room temperature within 7 h (Table 4). At the same time, the conversion of sulfides are 100% without exception. Similar to the oxidation of sulfide to sulfoxide, unsaturated double bonds are also tolerated during the reaction when aqueous hydrogen peroxide was used in great excess.

4. Conclusion

In conclusion, we have prepared recyclable catalysts of peroxotungstate immobilized on ionic liquid-modified silica that provide mild reaction condition and excellent chemoselectivity, which are easy catalytic systems for the selective oxidation of sulfides to their corresponding sulfoxides and sulfones with commercially available 30% aqueous hydrogen peroxide, an ideal oxidant. As we expected, the oxidation proceeded rapidly and completely within a short period of time with high yields. The catalysts could be easily separated from the reaction system and reused. To be the best of our knowledge, this is the first report on the application of ionic liquid-modified supported catalysts in the oxidation of sulfides.

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