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Temperature-Dependent Immobilization of a Tungsten Peroxo Complex That Catalyzes the Hydroxymethoxylation of Olefins

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A tungsten peroxo complex stabilized by the bidentate picolinato ligand has been synthesized and then immobilized successfully on imidazole-functionalized silica. The immobilized tungsten-based catalyst was employed as an efficient catalyst for the one-pot synthesis of β-alkoxy alcohols from olefins and methanol with H_2O_2. Regarding the catalyst evaluation and the results of characterization by the various methods, it was demonstrated that the immobilization of tungsten peroxo complex was highly temperature-dependent. The tungsten peroxo complex can dissociate and diffuse into the liquid phase at reaction temperature, resulting in a homogeneous reaction. Nevertheless, the catalytically active species was anchored on the imidazole-functionalized silica by hydrogen bonding as the temperature was lowered to 0 °C after the reaction, which thus offered a highly effective approach for recycling the catalyst for consecutive cycles. In addition, various olefins can be converted to the corresponding β-alkoxy alcohols with good conversion and selectivity under relative mild conditions by H_2O_2.

Introduction

Oxido-peroxido transition metal compounds have played an important role in the oxidation of various substrates, including olefins, alcohols, sulfides, and alkanes.[1–6] The catalytic activity of peroxide metal complexes is influenced by the type of metal atom and the number of peroxide ligands in the coordination sphere. Among these complexes, tungsten peroxo complex based oxidation systems with H_2O_2 have attracted much attention owing to their the high activity and inherent poor activity for the decomposition of H_2O_2.[7–9] The first example of transitition metal (Mo and W) peroxo complexes which were stabilized by the bidentate picolinato ligand was reported by Mares et al. in 1978.[10] They found that secondary alcohols can be transformed into ketones by the peroxo complexes in polar media under stoichiometric conditions or with H_2O_2 and with a moderate conversion. Then, Furia et al. reported the related oxido-bisperoxido complexes containing bidentate ligands and employed them in the oxidation of alcohols with a good catalytic activity.[11] Although various peroxo complexes have been used for different oxidation reactions, the immobilization and recycling of these catalytically active species still remain a huge challenge.

In view of the importance of β-alkoxy alcohols, which are used as valuable organic solvents, versatile synthons, fine chemicals, and pharmaceutical intermediates, the main protocol for the synthesis of β-alkoxy alcohols is the epoxidation of olefins and sequential alcoholysis of epoxides under basic or acidic conditions.[12–14] Obviously, the direct catalytic transformation of olefins into β-alkoxy alcohols offers a huge advantage over the two-step synthesis. Catalysts required for this transformation should be efficient in the olefin epoxidation and, as well, in the epoxide-ring-opening reaction by the alcohol. Nevertheless, only a few studies had reported the formation of the final β-alkoxy alcohols in one step, namely hydroxymethoxylation of olefin, starting from the olefin by using an appropriate oxidant and the alcohol. The reaction was first reported in 1957 and, up to now, this transformation has been performed by several catalysts under homogeneous and heterogeneous conditions.[15–17] However, these conventional systems have some drawbacks, like the limited substrate scope, poor recyclability of catalyst, and the harsh operating conditions. Therefore, the search for a highly active and recoverable catalytic system for hydroxymethoxylation under mild reaction conditions continues.

Compared with homogeneous catalysts, heterogeneous catalysts can be recovered from the reaction medium conveniently. Therefore, the immobilization of active oxido-peroxido transition metal compound on solid supports has attracted attention widely in the past decade. The usual approaches include immobilization on polymers, silica, and magnetic particles.[18–20] However, owing to the limited phase-transfer between solid catalyst and substrates, heterogeneous catalysts afford relatively poor yield compared with the homogeneous analogues. Thus, in order to combine the advantages of homogenous catalysts (activity and selectivity) with the facility of heterogeneous systems (recycling), some “smart catalysts” sensitive to

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temperature, CO_2, light, and pH. have been developed as well.[21–23] However, because the reaction is carried out normally at elevated temperatures and thus catalyst was typically filtered off at lower temperatures, the thermoregulated catalysts have attracted more attention recently. It has been reported that hydrogen bonding could be the ideal type of chemical bonding for reversible immobilization; hydrogen bonds form at low temperature but break at elevated temperature.[24,25] Thus, immobilization of catalytic species is possible through hydrogen-bonding interactions. In this context, a fiber-supported ionic liquid (IL) "release and catch" catalyst has been employed exclusively for a facile synthesis of bis(indolyl)methanes by Friedel–Crafts alkylation in water at room temperature.[26] Besides, a reversible catalyst immobilization via hydrogen-bonding-mediated self-assembly has also been reported for the atom transfer radical polymerization of methyl methacrylate (MMA). The catalyst was tethered on a diaminopyridine unit. A triple hydrogen-bond array formed between maleimide or thymine and diaminopyridine at room temperature but broke at elevated temperatures.[27]

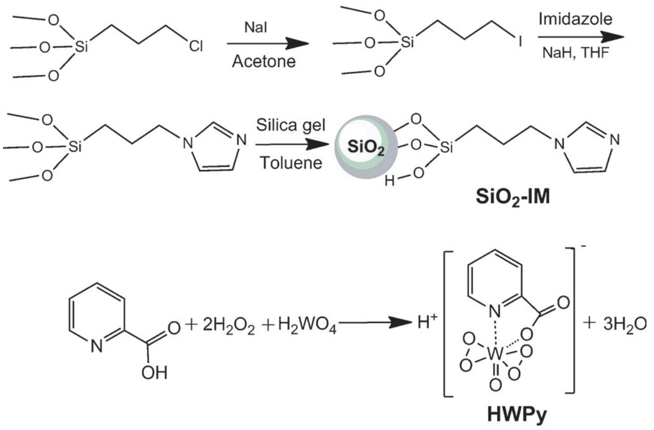
Regarding the above discussion and our previous research on the epoxidation of olefins,[28–31] in the present work we attempted to develop a highly efficient catalytic system for the hydroxymethoxylation of olefins, where the tungsten peroxo complex catalyzed the hydroxymethoxylation reaction in the homogeneous phase, but it can be also easily separated and recycled in a heterogeneous approach. Herein, we synthesized a tungsten peroxo complex stabilized by the bidentate picolinato ligand and then anchored it to imidazole-functionalized silica. It was found that the tungsten peroxo complex dissociated into the reaction medium from imidazole-functionalized silica and thus acted as "quasi-homogeneous catalyst" under reaction conditions, but anchored robustly to the functionalized silica when the temperature was lowered to 0 °C. The current procedure combines the advantages of both homogeneous catalysis with high activity and heterogeneous catalysis with easy recovery, and allows the direct transformation of various alkenes to β-methoxy alcohols using H_2O_2 as the oxidant, without the requirement of any other additives.

Results and discussion

Catalyst preparation and characterization

For the preparation of an imidazole-modified silica, 3-iodopropyltrimethoxysilane was first reacted with imidazole in the presence of NaH in THF under refluxing conditions (Scheme 1). Then the resulting *N*-(3-propyltrimethoxysilyl)imidazole was covalently anchored to silica by a convenient approach. The tungsten peroxo complex (HWPy) was synthesized according to the previous report.[10]

The successful grafting of *N*-(3-propyltrimethoxysilyl)imidazole onto silica was proved by ^{29}Si MAS NMR spectroscopy. As shown in Figure 1 a, the pure silica had two signals at $\delta = -110$ and -102 ppm, which were assigned to Si bonded to four siloxane units [(–OSi)$_4$] and Si bonded to three siloxane units and one silanol group [(-SiO)$_3$SiOH], respectively. For the functionalized SiO_2 (Figure 1 b), two new resonances at $\delta = -67$ and -58 ppm were observed, which were assigned to the T_3 and T_2 structural units, respectively. The appearance of T_3 and T_2 structural units confirmed that the functional group had attached to the surface of fumed silica successfully. And on the basis of N_2 adsorption–desorption isotherms, the BET surface area of SiO_2, SiO_2-IM, and the recovered SiO_2-IM-HWPy catalyst was 280.3, 239.1, and 185.2 $m^2 g^{-1}$, respectively. This indicated that after grafting with imidazole and HWPy, the functionalized silica material had a slightly decreased BET surface area. The reduction in surface area may result from the presence of the organic group and the polyoxometalate on the surface of silica. All these observation implied that imidazole ring was anchored covalently onto the surface of SiO_2 and also HWPy was loaded on SiO_2-IM.



Scheme 1. Preparation route of SiO_2-IM and HWPy.

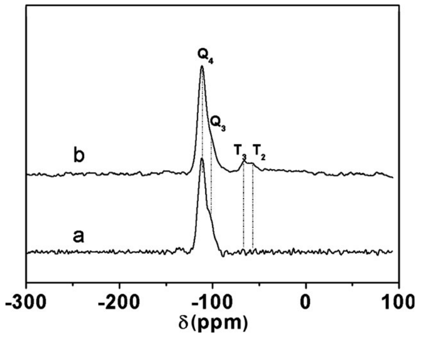


Figure 1. ^{29}Si CP-MAS NMR spectra of a) SiO_2; b) SiO_2-IM.

Then, X-ray diffraction patterns (XRD) of SiO_2, SiO_2-IM, and the recovered SiO_2-IM-HWPy catalyst were recorded (Figure 2). The broad peak around $2\theta = 20$–$30°$ is assigned to the amorphous silica. The XRD pattern of the SiO_2-IM did not differ from that of pure SiO_2. In addition, there were no characteristic peaks of HWPy in the XRD pattern of the spent SiO_2-IM-HWPy, which indicated that HWPy could be well dispersed on the surface of SiO_2-IM. Furthermore, from the SEM images shown in Figure 3, it can be seen that the functionalized silica particles and the recovered SiO_2-IM-HWPy showed more rough surface (Figure 3 b,c) than the parent silica (Figure 3 a), indicating that

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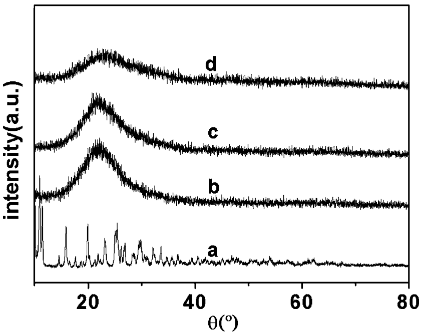

Figure 2. XRD patterns of a) HWPy; b) SiO_2; c) SiO_2-IM; d) SiO_2-IM-HWPy (recovered).

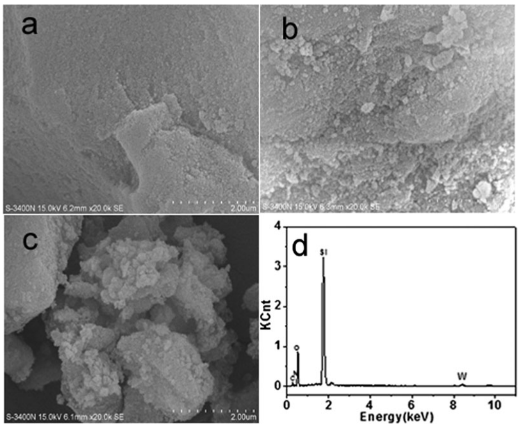

Figure 3. The SEM images of a) SiO_2; b) SiO_2-IM; c) the recovered SiO_2-IM-HWPy, d) EDS of the recovered SiO_2-IM-HWPy catalyst.

the surface morphology changed due to the immobilization of tungsten peroxo complex after the first run.

FTIR spectra of HWPy, SiO_2-IM, and the recovered SiO_2-IM-HWPy are shown in Figure 4. In the spectrum of SiO_2-IM, the characteristic peaks at 803 and 1000–1200 cm^{-1} were ascribed to the vibrations of Si–O–Si (sym) and Si–O–Si (asym), respectively; these peaks were also present in the spectrum of the recovered SiO_2-IM-HWPy. Additionally, the spectrum of HWPy (Figure 4a) showed characteristic peaks at 1663, 977, 883, 558, and 538 cm^{-1}, which were ascribed to the vibrations of C=O, W=O, O–O, $W(O_2)$(asym), and $W(O_2)$(sym), respectively. Interestingly, the band at 1519 cm^{-1} for SiO_2-IM is assigned to the imidazole ring stretch, which was blue-shifted to 1542 cm^{-1} in the recovered SiO_2-IM-HWPy. This change implied that the environment of the nitrogen atoms in the imidazole ring is very different due to the anchoring of HWPy to the imidazole; this observation coincides with previous research on the immobilization of phosphotungstic acid (PTA) onto imidazole-functionalized fumed silica.[32] In addition to the shift of the imidazole ring stretching, another strong piece of evidence that HWPy is anchored on the SiO_2-IM was the characteristic FTIR peak at 977 cm^{-1} assigned to the W=O in HWPy, which was shifted to 951 cm^{-1} in SiO_2-IM-HWPy.[33] Moreover, as shown in Figure 4c, the peak at 884 cm^{-1} assigned to the stretching of the peroxy group (–O–O–) was also observed, indicating that the catalytically active HWPy had been anchored on the surface of functional silicon successfully.

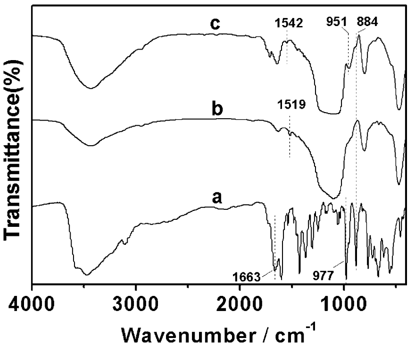

Figure 4. FTIR spectra of a) HWPy; b) SiO_2-IM; c) SiO_2-IM-HWPy (recovered).

Because only a small amount of the organic fraction (about 0.80 $mmol\,g^{-1}$) was loaded onto silica gel, the resonance signal in the solid-state ^1H NMR spectrum was weak. In additional experiments with solution-phase ^1H NMR spectroscopy butylimidazole (BIm) was used instead of SiO_2-IM to simulate the current SiO_2-IM-HWPy system. As shown in Figure 2S, the chemical shifts of protons (a, b, c) on the imidazole ring of BIm were $\delta=$ 7.6, 7.1, and 6.9 ppm, respectively. Nevertheless, upon the addition of HWPy to BIm in CD_3OD the signals of protons (c′, b′, a′) on imidazole ring were shifted significantly to $\delta=8.9$, 7.6, and 7.5 ppm, respectively. Meantime, it can be also observed that the chemical shifts of protons (d, e, f) in the alkyl chain of butylimidazole were moved downfield with the addition of HWPy. These ^1H NMR characterizations clearly indicated that the imidazole group can act as an H-bond acceptor and the tungsten peroxo complex (HWPy) as an H-bond donor.

Diffuse reflectance UV-visible spectra of SiO_2-IM, HWPy, and the recovered SiO_2-IM-HWPy catalysts are shown in Figure 3S. SiO_2-IM showed an absorption band at 224 nm which was attributed to imidazole, while HWPy showed an absorption band at 281 nm which was attributed to oxygen–tungsten charge transfer. However, for the recovered SiO_2-IM-HWPy catalyst this characteristic absorption band became sharper and was shifted to 271 nm.[34] This result suggests that a strong interaction exists between HWPy and SiO_2-IM, which is in accordance with the FTIR characterization.

Catalytic performance

First, the hydroxymethoxylation of styrene to the corresponding β-alkoxy alcohols at 60 °C for 12 h over different catalysts was performed and the reaction results are shown in Table 1. It can be seen that HWPy gave an excellent conversion and selectivity in CH_3OH, but it could not be recovered and reused after reaction due to the solubility of HWPy in CH_3OH even at 0 °C (Table 1, entry 1). Although HWPy was not as soluble in the mixed methanol/toluene (2:1) solvent system, the recyclability of HWPy was still very poor (Table 1, entries 2 and 3) owing to considerable leaching of W. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis indi-

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Table 1. Hydroxymethoxylation of styrene over different catalysts.[a]

Entry	Catalyst	Solv.	Conv. [%]	Sel. [%]				Leaching of W [ppm]	H_2O_2 eff. [%][g]
				Ether[b]	BA	BO	Diol		
1	HWPy	CH_3OH	99.0	90.0	6.8	2.0	1.2	miscible	87.4
2	HWPy	$CH_3OH+PhCH_3$[c]	98.5	82.1	9.5	5.5	3.0	7000	69.5
3	HWPy	$CH_3OH+PhCH_3$[d]	80.4	84.3	8.3	2.1	5.7	–	71.4
4	HWPy + SiO_2-IM	CH_3OH	90.3	83.0	12.5	2.5	1.0	530	87.1
5	HWPy + SiO_2-IM	$CH_3OH+PhCH_3$[c]	88.6	80.2	14.6	3.2	2.2	5.6	70.0
6	HWPy + SiO_2-IM	$CH_3OH+PhCH_3$[e]	53.4	55.5	39.5	4.5	1.0	4.5	70.5
7	HWPy + SiO_2-IM	$CH_3OH+PhCH_3$[f]	95.6	84.1	9.8	4.1	2.1	200	72.1

[a] Reaction condition: 0.05 g (0.12 mmol) HWPy, 0.15 g (0.12 mmol imidazole group) SiO_2-IM, 1 mmol styrene, 2 mmol 30% H_2O_2, 2 mL solvent, 60 °C, 12 h. [b] The main product was 2-methoxy-2-phenylethanol. [c] $V_{methanol}/V_{toluene}=2:1$. [d] Run 2 of entry 2, reaction time was 18 h. [e] $V_{methanol}/V_{toluene}=1:1$. [f] $V_{methanol}/V_{toluene}=3:1$. BA: benzaldehyde, BO: styrene oxide. [g] Remaining H_2O_2 was determined by potential difference titration of Ce^{3+}/Ce^{4+} (0.1 M of aqueous $Ce(SO_4)_2\cdot 4H_2O$). H_2O_2 effciency (%) = products (mol)/consumed H_2O_2 (mol) × 100.

cated that 7000 ppm of W was leached into decantate after the first run.

In order to immobilize HWPy more effectively, SiO_2-IM was added into the reaction mixture. Although the conversion and selectivity were slightly lower in methanol, in comparison with that in the absence of SiO_2-IM (Table 1, entries 1 vs. 4), the leaching of W was decreased to 530 ppm. However, when mixed methanol/toluene (2:1) was used as the reaction medium, the subsequent analysis of the decantate demonstrated that the leaching of W-based active species was approximately 5.6 ppm by ICP-AES (Table 1, entry 5), indicating that the leaching of W was negligible in the mixed solvents after reaction. In this case, the catalytic activity and selectivity were almost same as that in methanol media (Table 1, entries 4 and 5). Different ratios of methanol to toluene were also examined. Higher concentrations of toluene resulted in lower catalytic performance (Table 1, entry 6), while the introduction of more methanol afforded higher activity (Table 1, entry 7), but led to a considerable leaching of catalytically active species (about 200 ppm W was found in decantate). In addition, it was observed that most of the H_2O_2 was consumed for styrene oxidation. The introduction of toluene decreased slightly the H_2O_2 efficiency (Table 1, entry 4 vs. 5), while SiO_2-IM had almost no effect on H_2O_2 efficiency (Table 1, entry 2 vs. 5).

In the next step, the effect of the reaction parameters on the hydroxymethoxylation of styrene was investigated. As shown in Figure 5 a, as the reaction proceeded, the conversion of styrene increased continuously and full conversion was achieved after 18 h. On the other hand, the selectivity to the β-alkoxy alcohols remained constant and intermediate products such as styrene oxide were not detected in the course of the reaction. This implied that the rate of alcoholysis of the epoxide is so fast that epoxide is transformed to β-alkoxy alcohols as soon as it is generated. In order to further investigate the rate-limiting step of the reaction, styrene oxide was employed as the substrate under the optimized reaction conditions. The result showed that the styrene oxide was converted to the 2-methoxy-2-phenylethanol within 5 min with 96% conversion and 86% selectivity.

This indicated that the alcoholysis of the epoxide is much faster than the epoxidation of the olefin. In other words, the epoxidation is the rate-limiting step of the overall reaction and the epoxide was shown as an unstable intermediate under these reaction conditions. In addition, the effect of temperature on the reaction was also examined. As shown in Figure 5 b, the conversion of styrene increased with reaction temperature and remained unchanged at temperatures above 60 °C. Meantime, the selectivity to benzaldehyde was favored at lower reaction temperatures (<60 °C). When the reaction was carried out at low temperatures, the intermediate product styrene epoxide could not react with methanol quickly to afford 2-methoxy-2-phenylethanol, but rather underwent nucleophilic attack of H_2O_2 to yield the by-product benzaldehyde.[35] However, when the reaction was carried out at much higher temperatures (≥70 °C), direct oxidative cleavage of the C=C bond of styrene might happen and benzaldehyde was produced,[35] resulting in a slight increase of benzaldehyde selectivity (Figure 5 b). The results demonstrated that the reaction temperature affected both the conversion and the selectivity of the overall reaction, and therefore a suitable reaction temperature was crucial for the hydroxymethoxylation reaction.

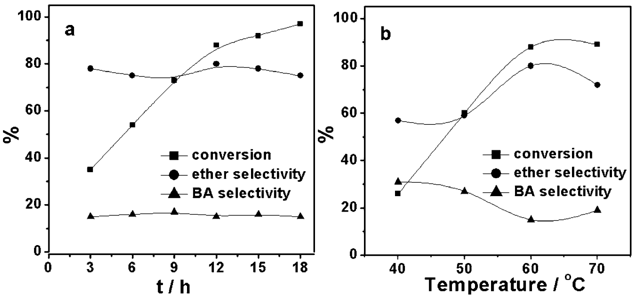

Figure 5. Time profile for the hydroxymethoxylation of styrene and the effect of temperature on the reaction. a) Reaction conditions: 0.05 g (0.12 mmol) HWPy, 0.15 g (0.12 mmol imidazole group) SiO_2-IM, 1 mmol styrene, 2 mmol 30% H_2O_2, 60 °C, 2 mL solvent ($CH_3OH/PhCH_3=2:1$); b) Reaction time was 12 h. (ether/2-methoxy-2-phenylethnol, BA: benzaldehyde).

Substrate generality and reusability of the catalyst

The optimized reaction conditions were then used to explore the substrate scope. Firstly, we mainly focused on the catalytic

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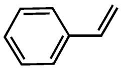
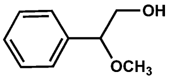
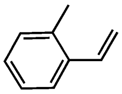
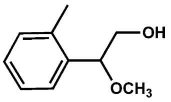
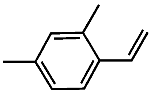
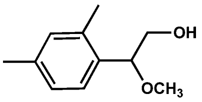
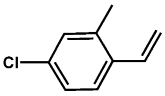
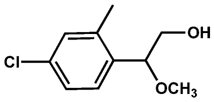
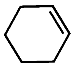
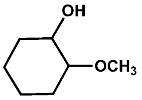
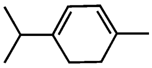
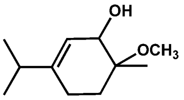
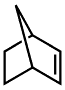
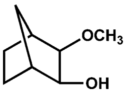
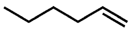
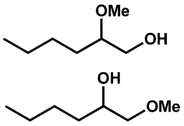
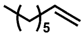
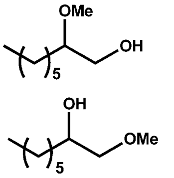
activities of styrene and its derivatives. As shown in Table 2, styrene, 2-methylstyrene, and 4-methylstyrene were converted into the corresponding β-alkoxy alcohols with approximately 90 % conversion and 75–80 % selectivity when the reaction was carried out for 12 h (Table 2, entries 1–3). However, the above substrates exhibited different reactivity in the following order: 4-methylstyrene > 2-methylstyrene > styrene when the reaction time was shortened to 6 h. Compared with the above three substrates, 4-chlorostyrene had a relatively low reaction rate with 87.6 % of conversion and 78.3 % selectivity after 24 h. That was because the synthesis of β-alkoxy alcohols proceeded through two steps: epoxidation of the olefin and alcoholysis of the epoxide to β-alkoxy alcohols, and the rate-limiting step seems to be the epoxidation of the olefin as a trace amount of epoxide was detected in the reaction. Since the epoxidation is an electrophilic addition reaction, the higher electron density at the double bond favored the epoxidation reaction. Therefore, the presence of the electron-donating group (-CH_3) at the *para* position or *ortho* position of styrene increased the reactivity of styrene, while the electron-withdrawing group (–Cl) at the *para* position of styrene decreased the reaction rate.

For cyclohexene, the conversion and selectivity were similar to that of styrene under the same reaction conditions (Table 2, entry 5). Terpinene and norbornene were also converted into the corresponding β-alkoxy alcohols with excellent conversion in short reaction time (Table 2, entries 6 and 7). The highly regioselective hydroxymethoxylation of the C=C bond in terpinene might result from steric hindrance. The existence of the isopropyl group was not favorable for the nucleophiles to attack the carbon atoms in the epoxide. It was worth noting that terminal olefins also could be converted into the corresponding β-alkoxy alcohols. For examples, 1-hexene and 1-octene were converted into the corresponding products with 81.2 %, 77.4 % conversion and 78.2 %, 83.1 % selectivity, respectively. Owing to the more substituted carbon in the intermediate adduct generated, there was slightly more primary alcohol product than secondary alcohol (Table 2, entries 8 and 9).

Table 2. Hydroxymethoxylation of various olefins over SiO_2-IM-HWPy catalyst.[a]

Entries	Substrates	Products	*t* [h]	Conv. [%]	Sel. [%][b]
1			6 12	54.1 88.6	75.3 80.2
2			6 12	67.3 89.5	74.4 78.3
3			6 12	81.2 91.4	76.2 80.2
4			12 24	44.8 87.6	68.4 78.3
5			18	91.9	78.3
6			2	98.0	55.2
7			5	93.1	65.9[c]
8			24	81.2	78.2 (56:44)[d]
9			24	77.4	83.1 (53:47)[d]

[a] Reaction conditions: 0.05 g (0.12 mmol) HWPy, 0.15 g (0.12 mmol imidazole group) SiO_2-IM, 1 mmol substrate, 2 mmol 30 % H_2O_2, 2 mL solvent ($CH_3OH/PhCH_3 = 2{:}1$), 60 °C, the products were all *trans* structures. [b] The main by-products were diols and aldehydes. [c] The ratio between *exo*- and *endo*-methoxy isomers was about 1:1. [d] The numbers in the parenthesis referred to the ratio of two isomers. The conversion and selectivity were determined by GC analysis.

Next, the recyclability of the SiO_2-IM-HWPy catalyst was investigated by choosing styrene as a model substrate under the optimized reaction condition. As shown in Figure 6, the catalyst could be reused at least five times only with a slight decrease of the catalytic activity due to the physical loss during the treatment. Actually, the leaching of W into solvent decreased gradually and can be negligible during the consecutive recycles. In order to understand whether HWPy was dissolved in the liquid phase under the reaction conditions, a fast hot filtration experiment was carried out at the reaction temperature. As shown in Figure 7, after reaction for 6 h, the reaction mixture was filtered. It was observed that the styrene in the filtrate continued to be converted to the corresponding β-alkoxy alcohols only with a slight decrease of reaction rate. The subsequent ICP-AES

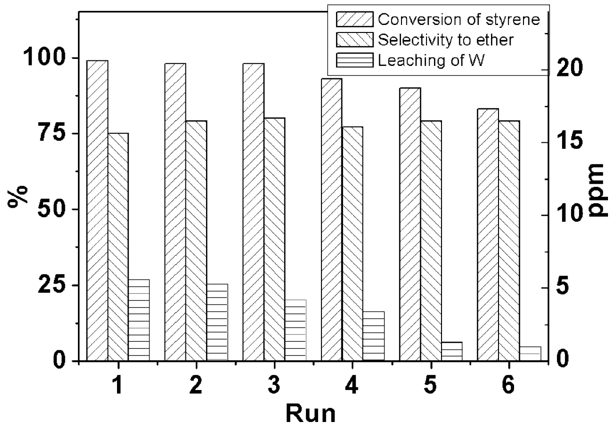


Figure 6. Recyclability of catalyst for hydroxymethoxylation of styrene. Reaction condition: 0.05 g (0.12 mmol) HWPy, 0.15 g (0.12 mmol imidazole group) SiO_2-IM, 1 mmol styrene, 2 mmol 30% H_2O_2, 2 mL solvent (CH_3OH/$PhCH_3=2{:}1$), 60 °C, 18 h. Ether (2-methoxy-2- phenylethnol) as a main product.

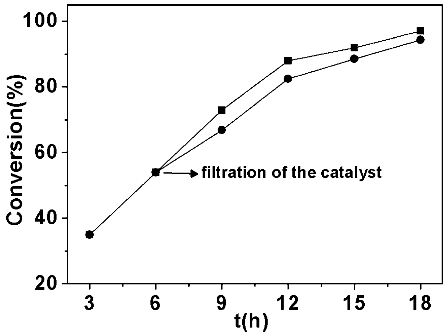


Figure 7. Time profile of reaction and fast hot filtration test of styrene catalyzed with SiO_2-IM-HWPy. Reaction condition: 0.05 g (0.12 mmol) HWPy, 0.15 g (0.12 mmol imidazole group) SiO_2-IM, 1 mmol styrene, 2 mmol 30% H_2O_2, 2 mL solvent (CH_3OH/$PhCH_3=2{:}1$), 60 °C. Solid solid represented the consecutive reaction without filtration, while solid circle reaction in the filtrate after filtration at 6 h.

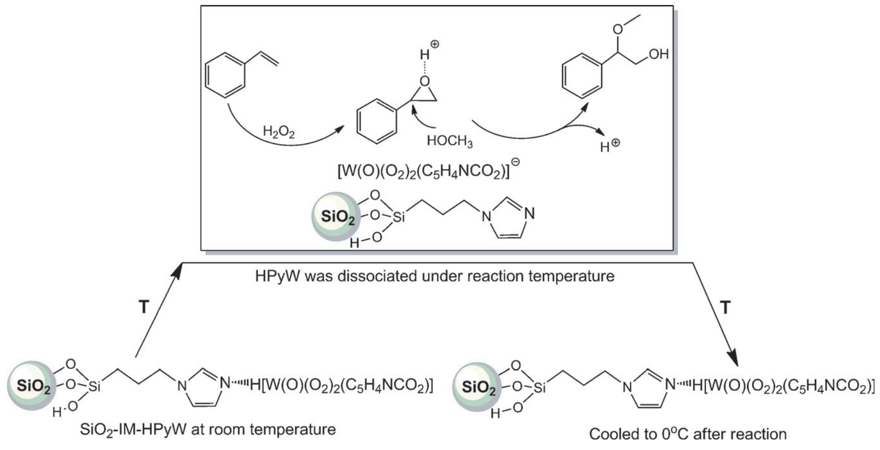
analysis showed that about 46.6% of the total W was dissolved in the liquid phase under reaction conditions. Thus it can be easily determined that the turnover frequency (TOF) of the catalyst was about 0.48 h^{-1} without filtration (filled circles in Figure 7). Nevertheless, the TOF of the filtrate was 0.85 h^{-1} after filtration (filled squares in Figure 7), which was almost twice that of the immobilized catalyst. Considering that almost a half of the total W was dissolved in the liquid phase, we can prove that the soluble active species plays an important role in catalyzing the hydroxymethoxylation reaction. This revealed that that active species could dissociate from SiO_2-IM under the reaction temperature. However, after the reaction, when the reaction mixture was cooled to 0 °C, the amound of dissolved W species was found to be negligible by ICP-AES analysis. This indicated that the W species was anchored effectively to the surface of the functionalized SiO_2 as the solution was cooled to 0 °C, resulting in almost no leaching of W-based active species.

Proposed mechanism for the catalytic system

As already described above, the one-pot synthesis of β-alkoxy alcohols from olefin requires two catalytic centers to complete the two different parts of reaction. In the present catalytic system, the tungsten-based peroxo complex (HPyW) was dissociated into the liquid phase under reaction conditions, and thus catalyzed the epoxidation process. Simultaneously, the dissociated proton further catalyzed the ring opening of the epoxide. After reaction, the tungsten-based peroxo complex was anchored effectively onto the surface of the modified silica through hydrogen-bond interactions. A detailed description of the reaction process is shown in Scheme 2. First, in the presence of H_2O_2, the anion of the tungsten peroxo complex was transformed into the active peroxo species, which epoxidized styrene to the styrene oxide, and this was the rate-limiting step of the whole reaction. Then, the epoxide could be protonated by the HWPy. Subsequently, methanol would attack the most stable benzyl carbocation from the backside, giving rise to the *trans* β-alkoxy alcohols by an S_N1 mechanism. The main by-product was benzaldehyde, which resulted from the nucleophilic attack of H_2O_2 to styrene oxide followed by cleavage of the intermediate hydroperoxystyrene, and the trace diols were produced from hydrolysis of styrene oxide.

Conclusion

In summary, we synthesized a tungsten peroxo complex-based stabilized by the bidentate picolinato ligand. Detailed characterization by elemental analysis, AES-ICP analysis, BET surface



Scheme 2. Proposed reaction mechanism for the hydroxymethoxylation of styrene in the mixed media.

area measurements, FTIR spectroscopy, NMR spectroscopy, and SEM confirmed that the tungsten peroxo complex was immobilized successfully onto the surface of silica. The immobilized tungsten peroxo complex was used as catalyst for the one-pot synthesis of β-alkoxy alcohols from olefin and methanol with H_2O_2. The catalyst can convert different kinds of olefins into the corresponding β-alkoxy alcohols with a good conversions and selectivities, and it was reused five times without a notable decrease in catalytic activity. Further investigation indicated that the catalytically active tungsten peroxo complex can dissociate from silica under the reaction temperature, resulting in a homogeneous reaction. However, the soluble W-based species was anchored robustly on silica as the temperature was decreased to to 0 °C. The proposed mechanism describes the simple temperature-dependent immobilization in detail. The mild reaction conditions and the simple procedure combined with the easy reuse of the catalyst and solvent make this method environmentally friendly and economical for the synthesis of β-alkoxy alcohols. Further work to expand and apply the catalyst is ongoing. This newly developed temperature-dependent immobilization provides a new strategy for the design and development of greener, more efficient, and economical chemical processes, and we believe that the current approach for immobilization of catalytically active species can inspire future research on homogeneous catalysis.

Experimental Section

General remarks

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. All solvents (A.R. grade) were dried with the standard methods. Silica gel was supplied by Qingdao Haiyang Chemical Reagents Co., Ltd, China. Commercially available H_2O_2 (30% in water), dichloromethane, acetone, toluene, methanol, ether was purchase from Sinopharm Chemical Reagent Co. Ltds. All reagents were commercially available and were used without further purification, unless otherwise stated. All ^{1}H NMR spectra were recorded on a Bruker Avance III 400 instrument (400 MHz for ^{1}H) by using $CDCl_3$ as solvent and Tetramethyl silane (TMS) as reference. Chemical shifts (δ) are given in parts per million and coupling constants (J) in hertz. Solid-state ^{29}Si/MAS NMR spectra were obtained on a Varian VAMRS 400 spectrometer. The XRD analysis was performed in D/MAX2550 VB/PC using CuKα radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 200 mA, scan rate 6 ° min^{-1}, scan area 10–80°. The elemental analysis of C, H, N was performed on an Elementar Vario El III Elementa and ICP-AES analysis of W on Vanan 710 instrument, respectively. FT-IR spectra were recorded at room temperature on a Niclet Fourier transform infrared spectrometer (Magna 550). Diffuse reflectance UV-visible measurements were recorded at room temperature with $BaSO_4$ as a reference on a Varian Cary 500 Spectrometer. A perkin Elmer Pyris Diamond was used in the current study for the thermogravimetric analysis (TGA) measurements. A constant heating rate of 10 °C min^{-1} was used in the flow of N_2. Scanning electron microscope (SEM) images were obtained on a JSM-6360LV microscope. BET surface areas were measured at the temperature of liquid nitrogen using a NOVA 4200e Analyzer. The products were analyzed by Shimadzu GC-2014 and GC-MS equipped with a HP-5 column (30 m, 0.25 mm i.d.) and an FID detector. For ^{1}H NMR and MS analysis, the crude products were purified by flash chromatography on a silica gel column using a mixture of petrol ether/ethyl acetate (5:1, v/v) as eluant.

Catalyst preparation

Synthesis of 3-iodopropyltrimethoxysilane

3-iodopropyltrimethoxysilane was prepared according to the reported procedures:[36] Under argon atmosphere, 36.9 g (0.246 mol) of sodium iodide were dissolved in 150 mL of dry acetone and then 48.9 g (0.246 mol) of 3-chloropropyltrimethoxysilane were added dropwisely under stirring. The mixture was heated to reflux under stirring overnight. Afterwards, the formed precipitate (sodium chloride) was filtered off and the solvent was removed under vacuum. The crude residue was washed with ether for three times and dried under vaccum. A yellowish liquid was obtained. Yield: 64 g (90%). ^{1}H NMR (400 MHz): $\delta = 0.74$ (t, 2H, Si-CH$_2$), 1.91 (q, 2H, I-CH$_2$-C*H*$_2$), 3.21 (t, 2H, I-CH$_2$), 3.57 ppm (s, 9H, Si-O-CH$_3$).

Synthesis of N-*(3-propyltrimethoxysilane) imidazole*

Under argon atmosphere, 4.8 g (0.12 mol) of sodium hydride was suspended in 150 mL of dry THF, and then the mixture was cooled to 4 °C with an ice bath and 8.2 g (0,12 mol) of imidazole were added over a period of 30 min. The suspension was stirred for 2 h until no release of hydrogen were observed. Then 26.12 g (0.09 mol) of 3-iodopropyltrimethoxysilane were added and the mixture was heated to reflux overnight. The orange suspension was filtered and the solvent removed under vaccum. Afterwards, 150 mL dry dichloromethane was added and the formed precipitate was filtered off. A transparent liquid was obtained. Yield: 12.5 g (60%). ^{1}H NMR (400 MHz): $\delta = 0.57$ (t, 2H, Si-CH$_2$), 1.86 (q, 2H, N-CH$_2$-C*H*$_2$), 3.51 (s, 9H, Si-O-CH$_3$), 3.93 (t, 2H, N-CH$_2$), 6.91 (s, 1H, N-CH-C*H*-N), 7.06 (s, 1H, N-C*H*-CH-N), 7.48 ppm (s, 1H, N-C*H*-CH-N).

Synthesis of imidazole-functionalized silica (SiO_2-IM)

SiO_2-IM was prepared by addition of *N*-(3-propyltrimethoxysilane) imidazole (2 g, 8.6 mmol) to a suspension of SiO_2 (4 g) in toluene (80 mL). The mixture was refluxed and stirred for 24 h. The solid materials were filtered off and washed with acetone and ether, and then dried under vacuum. Quantitative determination of the organic functional group covalently anchored onto the surface in the compound was performed using thermogravimetric analysis (TGA). Typically a loading at ca. 0.86 mmol g^{-1} for the organic functional group is obtained by TGA analysis (Figure 1S). Additionally, the elemental analysis of C, H, N for the functionalized silica also indicated 0.80 mmol g^{-1} organic functional group, which was consistent with that obtained by TGA analysis.

Synthesis of tungsten peroxo complex H [$W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$ (HWPy)

Hydrogen oxodiperoxo(pyridine-2-carboxylato) tungsten (VI) (HWPy) was prepared according to the literature.[10] A solution of pyridine-2-carboxylic acid (7.4 g, 60 mmol) in 10 mL of water was added to a solution of tungstic acid (15 g, 60 mmol) dissolved in 75 mL of 30% H_2O_2 chilled to 0 °C. The resulting solution was stirred overnight at room temperature. The volume of the solution was then reduced to 30 mL by evaporation under vacuum. Then, a white solid was precipitated and dried under vaccum. (74 %, Found: C, 15.6; H, 1.94; N, 2.93; W, 42.0 %. $C_6H_7NO_8W$ requires C, 17.8; H, 1.75; N, 3.45; W, 44.7 %).

Typical procedure for the transformation of olefins into β-alkoxy alcohols

The reaction was carried out in a 25 mL Schlenk flask equipped with a reflux condenser and a thermometer. After 0.05 g (0.12 mmol) HWPy and 0.15 g (0.12 mmol) SiO_2-IM were added, 1 mmol substrate, 2 mmol 30 % H_2O_2, and 2 mL of mixed solvent ($V_{methanol}/V_{toluene}=2{:}1$) was then charged into the Schlenk flask. The reation mixture was stirred at 60 °C for the desired time. Then the reaction mixture was cooled down to 0 °C, the HWPy catalyst was then self-precipitated and separated. After being washed with ether for three times and dried under vacuum, the recovered catalyst (SiO_2-IM-HWPy) was then separated easily for further characterization or the next catalytic recycle. The isolated liquid phase was further subjected to GC or GC-MS analysis for calculating conversion and selectivity to β-alkoxy alcohols.

The hot filtration experiments

After 0.05 g (0.012 mmol) HWPy, 0.15 g (0.012 mmol) SiO_2-IM, 1 mmol substrate, 2 mmol 30 % H_2O_2, and 2 mL of mixed solvent ($V_{methanol}/V_{toluene}=2{:}1$) was charged into the Schlenk flask sequentially, the mixture was heated up to reaction temperature and stirred vigorously. Aliquots of the samples were withdrawn at definite intervals and were analyzed by GC. In a parallel experiment, after the reaction proceeded for 6 h, the catalyst was rapidly filtered out with hot filter funnel from the reaction mixture under the reaction temperature, and then the remaining filtrate was allowed to continue on reaction.

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Keywords: β-alkoxy alcohols · functionalized silica · hydrogen bonds · heterogeneous catalysis · tungsten peroxo complexes

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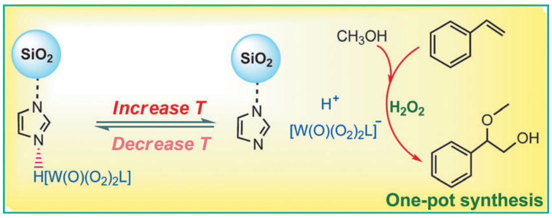
Temperature-Dependent Immobilization of a Tungsten Peroxo Complex That Catalyzes the Hydroxymethoxylation of Olefins



Running hot and cold: A tungsten peroxo complex (see picture) can dissociate and diffuse into the liquid phase at the reaction temperature, resulting in a homogeneous reaction. After reaction, the catalytically active species was anchored on the functionalized silica by hydrogen-bonding as the temperature was lowered to 0 °C. This offers an effective approach for catalyst recovery and recycling.

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