



Mesoporous SBA-15 materials modified with oxodiperoxo tungsten complexes as efficient catalysts for the epoxidation of olefins with hydrogen peroxide

Jianyuan Tang^a, Lei Wang^{a,b}, Gang Liu^a, Yan Liu^a, Yazhuo Hou^a, Wenxiang Zhang^a, Mingjun Jia^{a,*}, Werner R. Thiel^{b,**}

^a Key Laboratory of Surface and Interface Chemistry of Jilin Province, College of Chemistry, Jilin University, Qianjin Road 2699, Changchun 130012, China

^b Technische Universität Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str., Geb. 54, Kaiserslautern 67663, Germany

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ABSTRACT

A hybrid mesoporous SBA-15 material (**2a**) containing an oxodiperoxo tungsten complex of the type $[\text{WO}(\text{O}_2)_2\text{L}]$ (L = pyrazolylpyridine) was synthesized by a post-grafting route. The organic–inorganic hybrid catalyst was characterized by means of XRD, N_2 adsorption–desorption and FT-IR. The catalytic property of **2a** in the epoxidation of cyclooctene with H_2O_2 as the oxidant was investigated in comparison with other three kinds of hybrid tungsten containing SBA-15 materials bearing ethylenediamine, imidazole or 4,4'-bipyridine ligands. It was found that all oxodiperoxo tungsten catalysts were active at the reaction temperature of 55 °C with CH_3CN as solvent. However, only the catalyst with the pyrazolylpyridine ligand showed good recoverability and relatively high stability against leaching of active tungsten species. Moreover, this catalyst showed very high efficiency for H_2O_2 utilization, and its catalytic activity could be further improved by using solvent mixtures of CH_3CN and CH_3COOH .

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1. Introduction

The epoxidation of olefins is of great interest due to the importance of epoxides in the manufacture of both bulk and fine chemicals [1–2]. Recently, much attention has been drawn on developing novel catalytic processes based on inexpensive and eco-friendly oxidants (i.e. H_2O_2 , O_2) and efficient catalysts with high H_2O_2 efficiency and easy recoverability.

It was reported that various transition metal compounds (Mo, W, Fe, Mn, Re) are active catalysts for the epoxidation of olefins [3–11]. A few recent reports have shown that some tungsten-based catalytic systems were efficient for the epoxidation of olefins when using H_2O_2 as oxidant [12–15]. For example, Kamata et al. [6] reported that a silicotungstate compound exhibited high catalytic activity and efficiency in the epoxidation of olefins. Gao et al. [13] reported that mesoporous WO_3 -MCF materials showed good activity and recyclability in the epoxidation of cycloocta-1,5-diene. Kovalchuk et al. [14] designed a new approach to prepare heterogeneous epoxidation catalysts based on functionalized silica and heteropolyoxometalates. Tangestaninejad et al. [15] designed polymer-supported catalysts by immobilizing tungstenhexacarbonyl onto polystyrene, and found that

these catalysts were active and recyclable for the epoxidation of cyclooctene.

Previously, we reported a hybrid heterogeneous catalyst system, which was synthesized by covalently anchoring oxodiperoxo molybdenum chelate complexes of type $(\text{L-L})\text{MoO}(\text{O}_2)_2$ (L–L = 3-(2-pyridyl)-1-pyrazole) onto the surface of MCM-41 material [16]. This material was highly active and truly heterogeneous for the liquid-phase epoxidation of cyclooctene with *t*-BuOOH. The high stability against leaching of active species to liquid phase could be mainly attributed to the strong binding between the $\text{MoO}(\text{O}_2)_2$ unit and the chelate ligand [16,17].

Herein, a hybrid SBA-15 material (denoted as **2a**) containing oxodiperoxo tungsten chelate complexes, $[\text{WO}(\text{O}_2)_2\text{L}]$ (L = pyrazolylpyridine) was synthesized by a post-grafting route. For comparison, hybrid SBA-15 materials containing other ligands like ethylenediamine, imidazole, or 4,4'-bipyridine were additionally prepared (denoted as **2b**, **2c** and **2d**, respectively). The catalytic properties of all hybrid materials were investigated for the epoxidation of cyclooctene with H_2O_2 as the oxidant.

2. Experimental

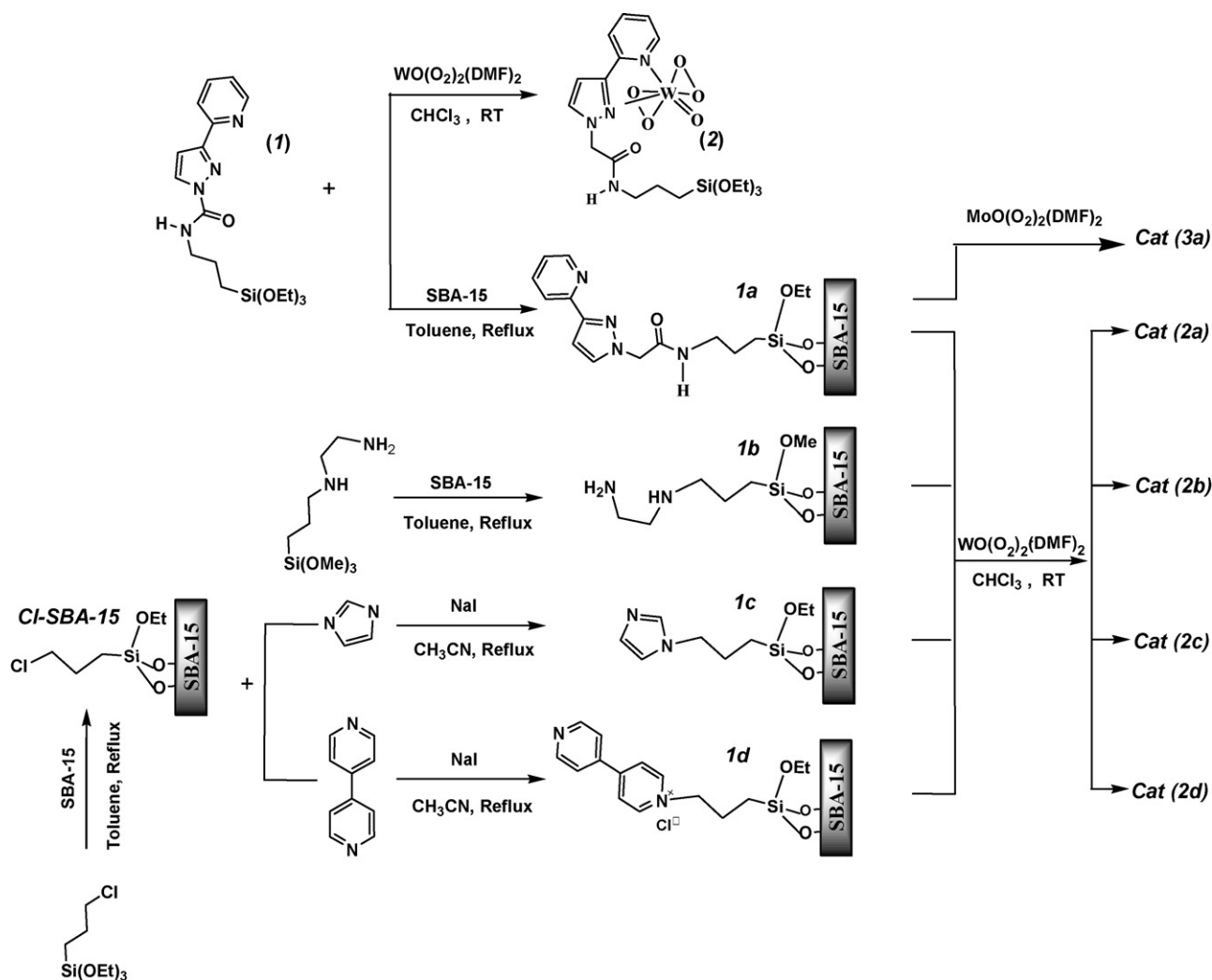
2.1. Synthesis of the mesoporous hybrid materials **1a** and **1b**

The mesoporous support SBA-15 (1.0 g), prepared by a literature method [18], was pre-activated by heating to 160 °C under vacuum for 3 h. After cooling and release of the vacuum,

* Corresponding author. Tel.: +86 431 85155390; fax: +86 431 88499140.

** Corresponding author. Tel.: +49 631 2052752; fax: +49 631 2054676.

E-mail addresses: jjamj@jlu.edu.cn (M. Jia), thiel@chemie.uni-kl.de (W.R. Thiel).



Scheme 1. Schematic representation for the preparation of hybrid mesoporous SBA-15 materials.

(3-(triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide (**1**) [19,20] (0.32 mmol in 40 mL of toluene) was added under a N_2 atmosphere and the mixture was heated to reflux for 24 h. The resulting solid (denoted as **1a**) was filtered, washed, Soxhlet-extracted with chloroform for 24 h, and dried in the vacuum at 70°C (see Scheme 1). The hybrid material **1b** [21] was synthesized analogously (see Scheme 1). Anal. found for **1a**: C, 5.57; H, 1.01; N, 1.50. Anal. found for **1b**: C, 2.77; H, 0.52; N, 0.71.

2.2. Synthesis of the mesoporous hybrid materials **1c** and **1d**

The hybrid materials **1c** and **1d** were synthesized according to literature procedures (Scheme 1) [22,23]. First, Cl-SBA-15 [24] was synthesized using the same procedure as for the synthesis of **1a** and **1b**. After that, Cl-SBA-15 (1.0 g, 0.32 mmol Cl), amine (0.64 mmol) and NaI (0.1 mmol) in 30 mL of CH_3CN were added to a 100 mL round bottom flask equipped with a magnetic stirrer. The mixture was heated to reflux for a few days. Finally, the solids were washed with a mixture of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (3:1) then with CH_3CN and finally were dried at 80°C (Scheme 1). Anal. found for **1c**: C, 2.90; H, 0.42; N, 0.81. Anal. found for **1d**: C, 5.03; H, 0.53; N, 0.71.

2.3. Preparation of $\text{WO}(\text{O}_2)_2 \cdot (\text{DMF})_2$

$\text{WO}(\text{O}_2)_2 \cdot (\text{DMF})_2$ was prepared according to a literature procedure [25–27]. Typically, 10 mL of a 6 M HCl solution

was dropped into an aqueous solution (25 mL) of 1.98 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (6.0 mmol) under stirring [28]. A yellow precipitate of $\text{H}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was isolated by filtration, and washed several times with water and ethanol. The precipitate was transferred quantitatively into a beaker, and 10 mL of 30% (wt.%) H_2O_2 was added under stirring at room temperature (25°C) to obtain a clear and colorless solution. After that, 1.6 mL of DMF was added under room temperature and the mixture was stirred for 2 h. The solvent was evaporated under vacuum in a rotary evaporator with a bath temperature of 65°C which resulted in a yellow solid. Then the resulting sample was washed with diethyl ether and dried at 80°C . Found: C, 15.87; H, 3.49; N, 6.67; W, 45.03%. Calc. for $\text{WO}(\text{O}_2)_2 \cdot (\text{DMF})_2$: C, 17.57; H, 3.42; N, 6.83; W, 44.86%.

2.4. Preparation of the oxidodiperoxo{(3-(triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide}tungsten(VI) (**2**)

0.61 g of ligand **1** (1.50 mmol) and 0.62 g of $\text{W}(\text{O}_2)_2 \cdot (\text{DMF})_2$ (1.50 mmol) were dissolved in 30 mL of dry CHCl_3 under N_2 atmosphere and stirred for 12 h at room temperature. The solvent was removed in vacuum, and the resulting yellow solid **2** was washed with diethyl ether and dried in a vacuum. Found: C, 34.29; H, 4.36; N, 8.42; W, 27.1%. Calc. for **2**: C, 34.0; H, 4.48; N, 8.36; W, 27.4%. For the tungsten complex **2**, the FT-IR spectrum is given in Figure S1 (see Supporting Information).

Table 1

Characteristics of support and catalysts, specific surface area, S_{BET} ($\text{m}^2 \text{g}^{-1}$); pore volume V_{BJH} ($\text{cm}^3 \text{g}^{-1}$); pore diameter D_{BJH} (nm); the C, H, N analyses of the hybrid materials **2a–2b**; $C(\text{W})$, initial concentration of W species (mmol g^{-1}).

Entry	Materials	S_{BET}	V_{BJH}	D_{BJH}	C%; H%; N%	$C(\text{W})$ (mmol g^{-1})
1	SBA-15	1348	2.09	7.5	–	–
2	2a	763	1.35	7.3	5.38; 0.98; 1.45	0.13
3	2b	426	0.78	6.7	2.74; 0.51; 0.70	0.04
4	2c	522	0.88	6.8	2.83; 0.41; 0.79	0.08
5	2d	482	0.84	6.7	4.98; 0.52; 0.70	0.04

2.5. Preparation of the mesoporous SBA-15 materials **2a–2d** modified with oxodiperoxo tungsten compounds

Compounds **1a–1d** (1.0 g) were stirred with 0.056 g (0.137 mmol) of $\text{WO}(\text{O}_2)_2 \cdot (\text{DMF})_2$ dissolved in 60 mL of CHCl_3 at room temperature for 24 h. The resulting samples **2a–2d** were filtered off, Soxhlet-extracted with CHCl_3 to remove untethered species and dried in vacuum. For the samples **2a–2d**, the data of C, H, N and W analysis are given in Table 1.

For comparison, a hybrid SBA-15 material containing $\text{MoO}(\text{O}_2)_2$ species (denoted as **3a**) was also prepared according to a previously reported procedure [16,17].

2.6. Characterization

Microanalyses for C, H, N were performed at the Perkin-Elmer 2400. Powder XRD diffraction patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA) using Ni-filtered $\text{Cu K}\alpha$ radiation. N_2 adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 423 K for 8 h before measurements. Specific surface areas were calculated using the BET model. Pore volumes are estimated at a relative pressure of 0.94 (P/P_0), assuming full surface saturation with nitrogen. Pore size distributions are evaluated from desorption branches of nitrogen isotherms using the BJH model. Transmission electron microscopy (TEM) images were taken with a Mic HITACHI I-8100 electron microscope operating at 200 kV.

FT-IR spectra were recorded on a Nicolet Impact 410 spectrometer. Typically, the dried sample was first pressed into a self-supporting wafer and placed into an infrared cell with KBr windows, then was pretreated at 423 K for 1 h under vacuum conditions prior to IR measurement.

Inductively coupled plasma atomic emission spectroscopy (ICP) analysis was conducted on a Perkin-Elmer emission spectrometer. Each 10–20 mg sample of vacuum-dried material was dissolved in 1 mL of boiling 5% KOH solution and then diluted to 10 mL with

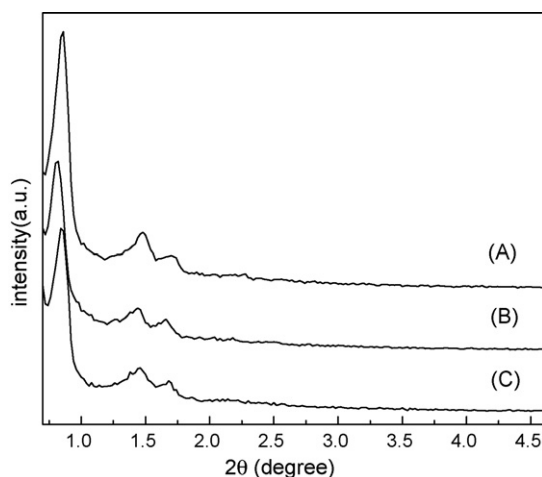


Fig. 1. Powder XRD patterns of SBA-15 (a); **1a** (b); **2a** (c).

deionized water. A 5 mL aliquot was acidified with 1 mL of concentrated HNO_3 before diluted to 10 mL with deionized water. Each solution was filtered through a polyethersulfone filter and then submitted for metal analysis [10].

2.7. Representative epoxidation conditions

The catalytic epoxidation of cyclooctene was carried out in a three-necked 50 mL flask equipped with a reflux condenser. In a typical reaction, 0.69 mL (5 mmol) of cyclooctene, 0.28 g of the catalyst suspended in 6 mL of the solvent, and 0.52 mL of 30% H_2O_2 (1 equiv.) were mixed. The reaction was then heated to a specific temperature and for a defined reaction time. After carrying out the reaction, the catalyst was filtered, washed with CH_3CN and CHCl_3 , dried under vacuum at 60 °C and reused directly without further purification. The course of the reaction was monitored by quantitative GC analysis. The catalytic activity for the epoxidation of cyclooctene was evaluated by the conversion of cyclooctene to cyclooctene epoxide.

3. Results and discussion

The powder XRD patterns of the two hybrid materials **1a** and **2a** and the neat SBA-15 support are shown in Fig. 1. The SBA-15 sample shows three peaks, indexed as the (100), (110) and (200) diffraction peaks associated with typical two-dimensional hexagonal symmetry of the SBA-15 material (Fig. 1a) [18]. For the

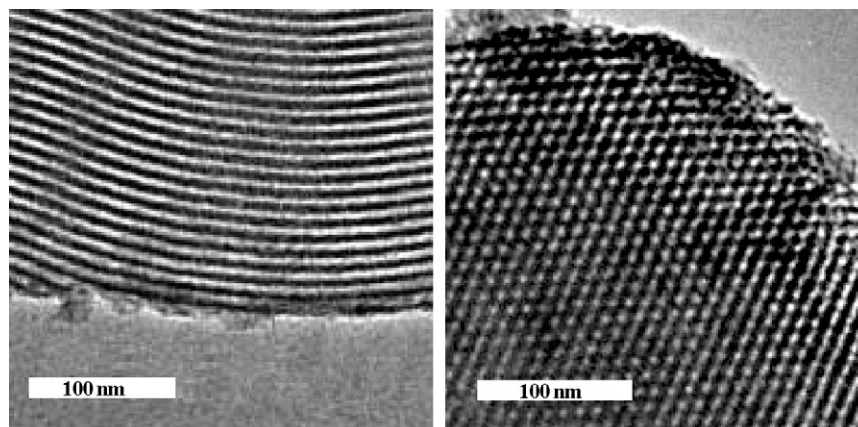


Fig. 2. Transmission electron micrograph (TEM) images of hybrid material **2a**.

hybrid materials **1a** and **2a**, the relative intensities of the prominent diffraction peak (1 0 0) decreased after introduction of the chelating ligand and the tungsten-containing complex (Fig. 1b and c). However, the main reflections of the XRD pattern can still be observed. According to related reference [16,29], the intensity reduction may be mainly due to contrast matching between the silicate framework and organic moieties which are located inside the channels of SBA-15. Similar XRD patterns were also obtained for other three hybrid materials **2b–2d** (see Fig. S2 in Supporting Information).

TEM images of the representative sample **2a** provide a direct visualization of well-ordered hexagonal arrays of 1D mesoporous channels particularly along the direction of the pore axis or in the direction perpendicular to the pore axis (see Fig. 2). This result is in good agreement with the conclusion withdrawn from the powder XRD patterns, and confirms that the characteristic pore dimensions and channel structures of the support materials remain intact after the introduction of tungsten complexes to the support SBA-15.

Fig. 3 shows the FT-IR spectra of SBA-15 support and four hybrid materials **1a–1d**. For SBA-15 support, the sharp band at 3740 cm^{-1} is attributed to the nonbonded surface Si–OH groups. For the hybrid materials **1a–1d**, the relative intensities of the Si–OH vibration decrease obviously in comparison with the support SBA-15, indicating that the condensation reaction to form Si–O–Si bonds between organosilane moieties and the surface Si–OH groups of SBA-15 has occurred under our experimental conditions. Moreover, in the region of $3200\text{--}2800$ and $1700\text{--}1500\text{ cm}^{-1}$, the spectra of the hybrid materials show some weak peaks, which should be due to the existence of organic ligands in the hybrid materials. On the basis of our previous work and the related literatures [16,17,21–24], we may conclude here that the corresponding organic ligands have been covalently grafted onto the surface of SBA-15.

The N_2 adsorption/desorption isotherms of the hybrid materials **1a**, **2a** and SBA-15 are shown in Fig. 4. Obviously, the hybrid materials **1a** and **2a** maintain the characteristics of type IV isotherms and show a uniform pore size distribution in the mesoporous region. Similar N_2 adsorption/desorption isotherms were also obtained for other three hybrid materials **2b–2d** (see Fig. S3 in Supporting Information). Compared to the support SBA-15, a pronounced decrease of the BET surface area, the pore volume, and the pore size occurred by the introduction of ligand and/or the tungsten complexes (Table 1).

The catalytic performances of various catalysts are shown in Table 2. When the oxidant H_2O_2 is used in combination with CH_3CN as solvent, all catalysts are active for the epoxidation of cyclooctene. The fresh catalyst **2b** shows the highest activity with 83% conver-

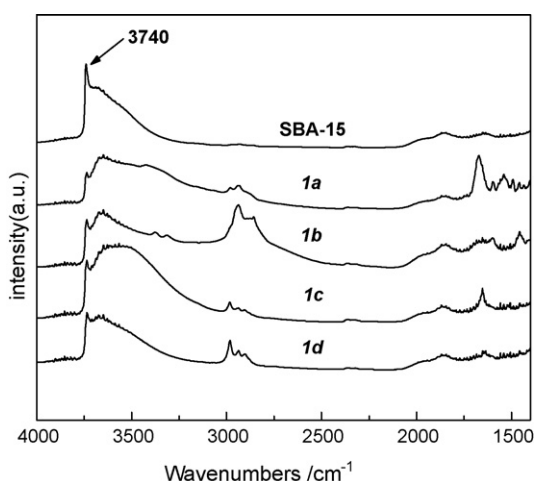


Fig. 3. FT-IR spectra of samples SBA-15 and the hybrid materials **1a–1d**.

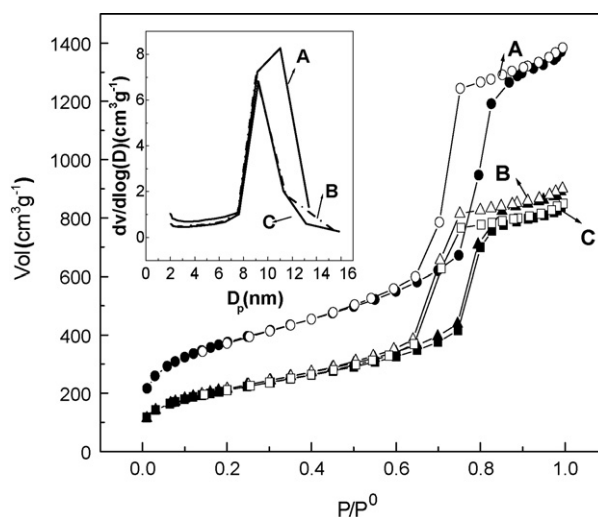


Fig. 4. N_2 adsorption/desorption isotherms at 77 K and pore size distribution profiles (inset) of various materials. (A): SBA-15; (B): **1a**; (C): **2a**.

sion of cyclooctene after 3 h ($\text{TOF } 143\text{ h}^{-1}$). Sample **2c** is also quite active (84% conversion after 6 h, $\text{TOF } 109\text{ h}^{-1}$), samples **2a** and **2d** show lower activities (76% and 65% conversion of cyclooctene after 10 h; $\text{TOF } 17\text{ h}^{-1}$ and 54 h^{-1}). However, the catalytic performances of the recycled catalysts differed significantly (Table 2). The catalytic activities of **2b–2d** decreased rapidly after the first run. But **2a** could be successfully recycled for six times without significant decrease of activity or selectivity under test conditions. The results of the ICP analysis show that the tungsten contents for the used catalysts just decrease slightly compared with the fresh one (Table 2). This indicates that leaching of active species should not be the only reason for the rapid deactivation of **2b–2d**. According to the literature [14], we suppose that the remarkable reduction of activity observed for **2b–2d** may mainly be attributed to the change of the coordinate environment of the active sites during the reaction.

To verify the heterogeneity of this catalytic process, a leaching test for catalyst was performed with **2a** (Fig. 5). The kinetic pro-

Table 2

Catalytic activities of various catalysts in the epoxidation of cyclooctene^a.

N	C(M) ± 0.01	C'(M) ± 0.01	Run	Time (h)	Conversion %	TOF (h^{-1})
2a	0.13		1	10	76	17
			2	10	75	16
			3	10	74	16
			4	10	75	17
			5	10	74	16
			6	10	73	16
2b	0.04	0.03	1	3	83	143
			2	3	41	94
			3	3	31	67
2c	0.08	0.08	1	6	84	109
			2	6	11	18
			3	6	0	0
2d	0.04	0.03	1	10	65	54
			2	10	37	31
			3	10	22	7.0
3a	0.13	0.13	1	10	35	7

Note: N, catalyst reference; C(M), initial concentration of M (M = W or Mo) species (mmol g^{-1}); C'(M), concentration of M species in spent sample after last run (mmol g^{-1}); conversion of cyclooctene; TOF, average turnover frequency in first hour per active site.

^a Catalysis conditions: reaction temperature $55\text{ }^\circ\text{C}$, 5 mmol of cyclooctene, 5 mmol of H_2O_2 in hydrous solution, 0.28 g of catalyst and 6 mL of CH_3CN , reaction time 3–10 h. In all cases, the selectivity towards epoxy cyclooctane was about 100%.

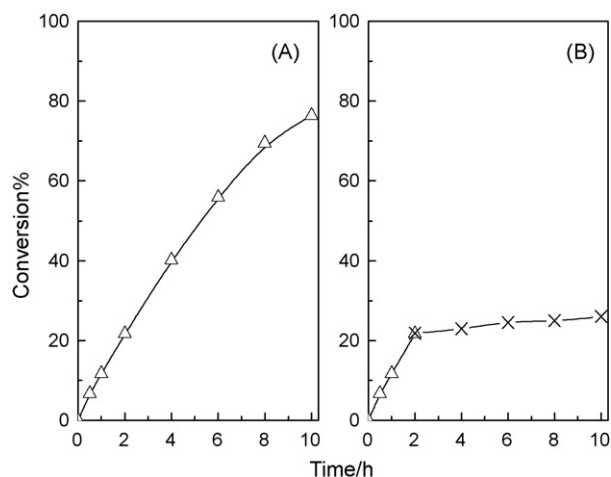


Fig. 5. (A) Kinetic profiles of epoxidation of cyclooctene with H_2O_2 over **2a** (Δ). (B) Heterogeneous reaction check for **2a** (Δ), by continuing the reaction after removing the catalysts **2a** (\times) by filtration at reaction temperature.

file of epoxidation of cyclooctene with CH_3CN as solvent over **2a** catalyst is shown in Fig. 5A. In a duplicate reaction, it was found that cyclooctene could just be converted at a very low rate in the solution after removing the catalyst (**2a**) by filtration at the reaction temperature (Fig. 5B). These results suggest that only trace of active W species have been leached from the hybrid mesoporous host, implying that the large majority of the catalysis is carried out by truly heterogeneous W catalyst.

For comparison, the catalytic property of corresponding Mo-containing catalyst (denoted as **3a**, see Scheme 1.) in the epoxidation of cyclooctene with H_2O_2 as oxidant is also studied under an identical reaction conditions. After 10 h, a 35% conversion of cyclooctene could be obtained, which is much lower than the corresponding W-based catalyst (**2a**). These results suggest that the tungsten-containing catalyst **2a** shows superior activity for the activation of H_2O_2 . In general, it is known that the chemistries of molybdenum and tungsten oxides are quite similar in many cases. However, some differences in the physicochemical properties are still existed between these two compounds, such as the Pauling electronegativities (Mo: 2.20; W: 2.36), the ionic radii (Mo^{6+} : 0.59 and W^{6+} : 0.60) and the Lewis acid strength of the cations [30]. Such difference may bring some considerable influence on the catalytic performances of the resultant Mo or W-complexes. For example, Jimtaisong and Luck reported recently that the homogeneous $\text{W}(\text{O})(\text{O}_2)_2\text{dppmO}_2$ catalyst showed much higher activity than the corresponding Mo-based catalysts for the epoxidation of cyclooctene with H_2O_2 as oxidant [31].

Table 3
Epoxidation of cyclooctene with aqueous H_2O_2 catalyzed by **2a** (reaction time: 4 h).

N	C(W), ± 0.01	C(W), ± 0.01	Temperature ($^\circ\text{C}$)	Solvent	Run	Conversion %
1	0.13	0.13	35	CH_3CN	1	11
2	0.13	0.13	55	CH_3CN	1	40
3	0.13		70	CH_3CN	1	82
4					2	76
5					3	68
6		0.09			4	62
7	0.13	0.13	55	$\text{CH}_3\text{COOC}_2\text{H}_5$	1	8
8	0.13		55	$\text{CH}_3\text{CH}_2\text{OH}$	1	63
9					2	31
10					3	29
11					4	27
12		0.7			5	25

Note: C(W), initial concentration of W species (mmol g^{-1}); C(W), concentration in spent sample after the last run (mmol g^{-1}). Catalysis conditions: 5 mmol of cyclooctene, 5 mmol of H_2O_2 /in hydrous solution, 0.28 g of catalyst and 6 mL of solvent. In all cases, the selectivity towards epoxycyclooctane was about 100%.

The influence of the reaction temperature and the solvent on the catalytic properties of **2a** was also investigated (Table 3). With CH_3CN as the solvent, the conversion of cyclooctene increased gradually from 11 to 82% when the reaction temperature increased from 35 to 70°C (Table 3, entries 1–3). However, at 70°C , the recoverability of **2a** was not as good as at 55°C .

Moreover, the results presented in Table 3 (see entries 2, 7, 8) also suggest that the catalytic epoxidation with **2a** is solvent dependent. At the reaction temperature of 55°C , ethanol gave the highest conversion of cyclooctene (63%), while with $\text{CH}_3\text{COOC}_2\text{H}_5$ only poor yields of the epoxide were obtained (8%). However, with ethanol as the solvent, the recoverability of **2a** was poor, since the catalytic activity decreased considerably with increasing the number of recycling experiments (Table 3, entries 8–12). Similar results have been reported by Jimtaisong and Luck for the epoxidation of cyclooctene with the $\text{W}(\text{O})(\text{O}_2)_2\text{dppmO}_2$ catalyst [31]. They suggested that the decrease of the catalytic activity may be due to a substitution of the ligands by $\text{CH}_3\text{CH}_2\text{OH}$. In our case, this should result in soluble tungsten species and serious leaching of the active sites. As shown in Table 3, the tungsten content in the hybrid material was strongly reduced after the fifth cycle with ethanol as the solvent. This can be a hint that with ethanol, the epoxidation is not a heterogeneous one and that the supported tungsten complex solely serves as a reservoir for active tungsten sites in solution.

Previously, it was reported that the addition of some organic acids (e.g. acetic acid) into the reaction system might be beneficial to design efficient and synthetically useful systems for olefin epoxidation [8,32]. Therefore the catalytic performance of **2a** was investigated for the epoxidation of cyclooctene in the presence of acetic acid. Fig. 6A shows the effect of the addition of acetic acid on the activity of **2a**. Using a mixture of CH_3CN and CH_3COOH (volume ratio: 1:2) as the solvent, the conversion of cyclooctene increased to 76% after 10 h at a relatively low temperature of 35°C . Thus the activity of the system is higher than that using CH_3CN as solvent (21%, Table 3, entries 1). Moreover, the catalytic properties of the recycled **2a** catalyst did not change significantly compared to the fresh sample (Fig. 6A), indicating the excellent recoverability of this system.

The heterogeneity test for catalyst **2a** was also performed when using the mixture of $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$ as solvent (Fig. 6B). It should be mentioned firstly that a blank reaction (without adding any catalyst) using the mixed solvent gave a conversion of cyclooctene of about 3% after a reaction time of 2 h, and of 12% after 10 h. With **2a** as the catalyst, the conversion of cyclooctene reached 18% after 2 h. After removing the catalyst by filtration, the conversion of cyclooctene increased to 28% during the following 8 h. Taking the result of the blank reaction into account, it is reasonable to assume that no obvious leaching of the active catalytic species occurs during the reaction.

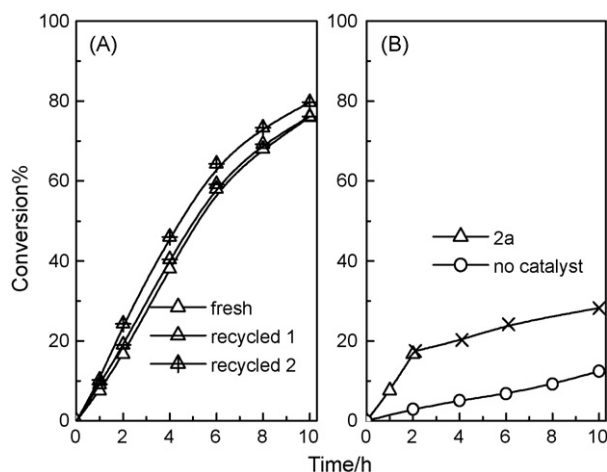


Fig. 6. (A) Catalytic activity and recoverability of **2a** for the epoxidation of cyclooctene with H_2O_2 in the presence of mixed solvent of CH_3CN and CH_3COOH . (B) Heterogeneous reaction check for **2a** (Δ), by continuing the reaction after removing the catalysts **2a** (\times) by filtration at reaction temperature. Reaction conditions: 5 mmol of cyclooctene, 5 mmol of 30% H_2O_2 , 0.28 g of **2a** (substrate/"W" ratio 13), and 6 mL of a 1:2 $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$ mixture; reaction temperature 35 °C.

The efficiency of H_2O_2 utilization was additionally investigated for **2a–2d** by using reaction conditions reported by Kamata et al. [6]. In this case, a relatively low molar ratio of $\text{H}_2\text{O}_2/\text{olefin}$ (1:5) was adopted since it is more suitable for studying such feature. According to the yield of epoxycyclooctane as well as the consumed amount of H_2O_2 , the efficiency of H_2O_2 utilization can be calculated. It can be seen that all of the catalysts exhibit high efficiency of H_2O_2 utilization (>85%). Among them, **2a** shows the highest H_2O_2 utility under the test conditions, and the catalytic epoxidation could proceed with >99% selectivity to epoxide, and >99% efficiency of H_2O_2 utilization over this catalyst (Fig. 7).

Previously, it was known that many transition metal compounds showed unfavorable decomposition of H_2O_2 in the epoxidation reaction, thus resulting in a low efficiency in H_2O_2 utilization [2,33,34]. A few recent literatures have reported that W-based catalysts exhibit relatively high H_2O_2 efficiency for the epoxidation of olefins by changing the structure or the coordination environments of W species [13,35]. For instance, Gao et al. proposed that

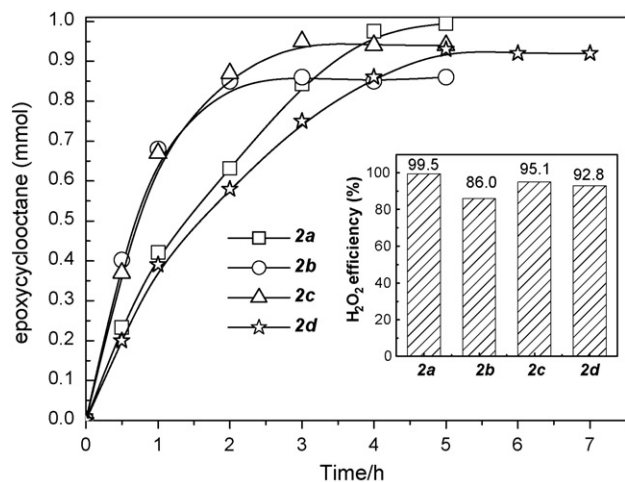


Fig. 7. Epoxidation of cyclooctene catalyzed by **2a–2d** with H_2O_2 and the efficiency of H_2O_2 utilization (inset) of the materials **2a–2d**. Reaction conditions were as follows: cyclooctene (5 mmol), catalyst (0.28 g), 30% aqueous H_2O_2 (1 mmol), and CH_3CN (6 mL), at 55 °C. H_2O_2 efficiency (%) = [product (epoxycyclooctane) (mol)/consumed H_2O_2 (mol)] \times 100.

the presence of highly isolated tetrahedral $[\text{WO}_4]^{2-}$ species and the unique pore structure of $\text{WO}_3\text{-MCF}$ should be responsible for the high activity and efficiency of H_2O_2 utilization [13]. Our previous work has shown that the chelate ligand of pyrazolopyridine is quite suitable to form active and stable Mo-based epoxidation catalysts due to the special coordination ability of this ligand [16,17]. In the present work, we suppose that the nice features of **2a** could also be mainly assigned to the formation of a suitable coordination interaction between the chelate ligand and the $\text{WO}(\text{O}_2)_2$ fragment. Besides, the structure and surface properties of SBA-15 support may also play a positive role in improving the catalytic performance of the hybrid material.

4. Conclusion

Hybrid mesoporous SBA-15 materials containing oxodiper-oxo tungsten complexes ($[\text{WO}(\text{O}_2)_2\text{L}]$, where L = pyrazolopyridine, ethylenediamine, imidazole, 4,4'-bipyridine) show good activity for the epoxidation of cyclooctene with H_2O_2 as oxidant. The catalyst bearing pyrazolopyridine ligand (**2a**) exhibits relatively high recoverability, stability and very high efficiency of H_2O_2 utilization under optimized conditions. Furthermore, the epoxidation activity of **2a** catalyst could be considerably improved by using the mixed solvent of CH_3CN and CH_3COOH (volume ratio of 1:2), and **2a** catalyst could catalyze the reaction even at a temperature as low as 35 °C, and no apparent leaching of active tungsten species could be detected under such mild reaction conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.07.018.

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