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Synthesis and catalytic properties of macroporous SiO₂-coated CNTsieve-composite-supported 12-tungstophosphoric acid catalysts with dual pore structure for the Baeyer–Villiger oxidation of cyclic ketones under microwave irradiation



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ABSTRACT

Carbon nanotube sieves (CNTs-S) with a flutelike shape were synthesized by cutting and perforating using a chemical oxidation etching method. Using the obtained CNTs-S as a hard template, SiO₂-coated CNTs-S dual pore structures (CNTs-S@SiO₂) were formed. Finally, tungstophosphoric acid was supported on CNTs, CNTs-S, and CNTs-S@SiO₂ matrices by the incipient wetness method to obtain the corresponding supported catalysts $PW_{12}/CNTs$, $PW_{12}/CNTs$ -S, and $PW_{12}/CNTs$ -S@SiO₂. The results showed that obtained $30\% PW_{12}/CNTs$ -S and $30\% PW_{12}/CNTs$ -S@SiO₂ catalysts in 30 wt% dipping solution had the best catalytic performance for Baeyer-Villiger oxidation of cyclic ketones by H_2O_2 . The conversion of cyclohexanone was 94% and 91%, respectively, in 5 min under microwave irradiation. Cyclopentanone and adamantanone approached quantitative conversion and the selectivity of corresponding lactones reached 100%. The dual pore structure catalyst showed very excellent cyclic stability.

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1. Introduction

The Baeyer–Villiger oxidation reaction (B-V reaction), one of the most important organic reaction types, has been intensively studied and applied [1]. This reaction allows efficient synthesis of important esters or lactones directly from ketones [2]. Especially, lactones are important intermediates for preparing many valuable polymers, medicines, insecticides, and natural products [3–8].

As is known, the most commonly used oxidants in B-V reactions are organic peroxide acids [9,10], but these substances usually are flammable and explosive and their use poses a safety risk. Further, use of peroxide acids will produce equimolar carboxylic acid waste. Therefore, scientists have been trying to use H_2O_2 to replace organic peroxide acids as environmentally friendly oxidants [3,5,6,11–13].

12-Tungstophosphoric acid (H_3PW_{12}) is a commonly used highly effective catalyst for the B-V reaction, but the poor separation and cycling performance of the homogeneous catalyst limit its

* Corresponding author. E-mail address: yangw@nwnu.edu.cn (W. Yang). practical applications. Thus, solid-matrix-supported catalysts are a necessary choice. Porous materials are preferred matrix materials owing to their high specific surface area and high affinity.

The main drawbacks of microporous materials are low adsorptive capacity and high mass transfer resistance [14]. Macroporous materials possess high permeability and high mass transfer rates, but poor selectivity for solute molecules [15]. Mesoporous structures have relatively higher specific surface area, medium aperture, and controlled hole-wall composition by comparison, but its permeability for larger quest molecules is unsatisfactory. It can be predicted that catalysts with mesopore–macropore dual structure can effectively improve catalytic activity and selectivity.

There has been a report of the use of carbon nanotubes (CNTs) to catalyze B-V reactions [16]. But conveniently obtained CNTs have sealed ends and dense hole-walls; when they are used as catalyst supporters, the channels are very easily blocked so that the catalytic activity will change for the worse. Thus the structural modification for CNTs is very necessary.

In this paper, we first prepared flutelike carbon nanotube sieves (CNTs-S) with medium hole aperture of the CNTs (\sim 20 nm) as raw materials by cutting and drilling holes in walls by a chemical etching method; then we synthesized macroporous silicon oxide (i.d.



50 nm) as a coating for CNTs-S composite (CNTs-S@SiO₂); and last we successfully obtained a composite-supported 12tungstophosphoric acid catalyst by a simple dipping method. The catalyst showed excellent catalytic performance for B-V oxidation of cyclic ketones. The results also displayed that microwave irradiation could remarkably improve the reactions.

2. Experimental details

2.1. Reagents and apparatus

Multiwall carbon nanotubes (MWCNTs) were obtained from Shenzhen Nanoscale Harbor Co., with pipe diameter 10-30 nm and length 0.1-200 µm. Tetraethoxysilane (TEOS, AR) was purchased from BASF, Tianjin. 3-Aminopropyltriethoxysilane (APTES, AR) was bought from Tianjin Chunjing Chemical Co. Cyclohexanone (AR) was acquired from Yaohua Chemical Regents Co., Tianjin. Cyclobutanone (98%), cyclopentanone (99%), 2-methyl cyclohexanone 95%), 4-methyl cyclohexanone (98%), 2- tert-butyl cyclohexanone (98%), 4-tert-butyl cyclohexanone (98%), adamantanone (98%), and menthone (98%) were purchased from ABCR GmbH & Co. KG, Germany. Di-isopropylketone (AR) and diisobutylketone (AR) were obtained from Union Chimique Belge, Belgium. Hexadecyltrimethylammonium bromide (CTAB, AR), mesitylene (TMB, CP), and H₂O₂ (30%, AR) were bought from Sinopharm Chemical Reagent Co. H₃[PW₁₂O₄₀]·xH₂O (H₃PW₁₂, AR) and Na₃[PW₁₂O₄₀]·*x*H₂O (Na₃PW₁₂, AR) were acquired from Aladdin, Shanghai. Other reagents were of analytical grade and used without further purification.

IR spectra were measured by a Digilab Merlin FTS 3000 FT-IR spectrometer (USA). Raman spectra were observed with a Bruker RFS100/S FT Raman spectrometer (Germany) with an excitation wavelength of 1065 nm. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) curves were recorded by a Perkin Elmer Pyris Diamond TG/DTA 6300 thermal analyzer (USA) with a

heating rate of 10 °C/min under N₂. XRD patterns were acquired by a Shimadzu XRD 6000 X-ray diffractometer (Japan) with CuK α irradiation (λ = 1.5406 nm), tube voltage 40 kV, and tube current 30 mA. X-ray photoelectron spectroscopy (XPS) was carried out with a Physical Electronics FHI-5702/ESCA/SAM multifunctional X-ray photoelectron spectrometer (USA) with MgK α as excitation source and C1s binding energy 284.6 eV as internal standard. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution of the samples were measured by an N₂ adsorption-desorption technique using a Micromeritics ASAP2010 surface area and porosity analyzer (USA). A JEOL JSM-6701F ultra-high-resolution FE scanning electron microscope (SEM, Japan) was employed to observe sample surface morphologies and to obtain surface compositions (EDS). Pore morphologies of the samples were observed by a JEOL JEM 1200 EX transmission electron microscope (TEM, lapan).

A SRJX2229 tubular furnace (Experimental Electric Furnace Factory of Changsha, China) was used for template removal of the materials and a Midea microwave stove (Guangzhou) was exploited to improve the catalytic reaction.

A Hewlett–Packard GC6890/MS5793 gas chromatograph mass spectrometer was used to identify the oxidation products of the B-V reaction (30 m × 0.53 mm × 0.25 µm column, mass detector, He 1.0 µL/min, injection temperature 280 °C, programmed temperature rate 15 °C/min). A Shimadzu GC-2010 gas chromatograph (15 m × 0.53 mm × 0.25 µm Rtx-1 column, FID detector, N₂ 30 mL/min, air 400 mL/min, sample size 0.2 µL) was used to evaluate the catalytic activity of the synthesized catalysts.

2.2. Preparation of CNTs and CNTs-S supported tungstophosphoric acid catalysts

2.2.1. Purification of MWCNTs and preparation of CNTs-S

According to Ref. [27], 0.5 g of MWCNTs was put into a sand core crucible, which was transferred into a sealed Teflon-lined



Scheme 1. Preparation procedures for the catalysts PW12/CNTs-S and PW12/CNTs-S@SiO2

autoclave with 5 mL concentrated HNO₃, and then the temperature was kept at 160 °C for 5 h. After it was washed with distilled water and absolute ethanol and dried at 80 °C in a vacuum oven for 5 h, purified CNTs were obtained. Similarly, by keeping the temperature at 200 °C for 3 h, CNTs-S would be obtained.

2.2.2. Preparation of CNTs- and CNTs-S-supported tungstophosphoric acid catalysts

The incipient wetness method [28] was used to prepare the target catalysts. The typical preparation process was as follows: A weight of 0.5 g of CNTs or CNTs-S was dried at 100 °C in a vacuum oven overnight in a glass dish, into which tungstophosphoric acid solution with a given concentration (10, 20, 30, and 40%) was dripped until the samples were just covered. The mixtures were allowed to stand for 4–5 h; then the redundant solution was blotted carefully with filter paper and allowed to stand for 48 h more. Last, the samples were dried at 100 °C overnight and calcined at 300 °C for 4 h in a tubular furnace to obtain the supported catalysts, which were respectively labeled as w%PW₁₂/CNTs and w% PW₁₂/CNTs-S (w% was the mass concentration of tungstophosphoric acid).



Fig. 1. IR spectra of the samples. (A) CNTs (a), CNTs-S (b), and 30%PW₁₂/CNTs-S (c); (B) CNTs-S@SiO₂ (d) and 30%PW₁₂/CNTs-S@SiO₂ (e).

2.3. Preparation of SiO₂-coated CNTs- and CNTs-S-supported tungstophosphoric acid catalysts

2.3.1. Preparation of SiO₂-coated CNTs and CNTs-S composites

A quantity of 0.1 g of CNTs (or CNTs-S) and 1 g of CTAB were mixed, added into 30 mL deionized water, and ultrasonically dispersed for 1 h; then the mixture was added into 80 mL absolute ethanol and continually ultrasonically dispersed for 2.5 h more. A quantity of 2 mL of ammonia and TEOS solution (1 mL TEOS + 40 mL ethanol) were successively dripped into the above mixture and continuously stirred to react for 13 h. After the reaction was finished, the mixture was centrifugally separated, washed three times with ethanol, and dried at 80 °C in a vacuum oven for 12 h. The presynthesized products were extracted twice with 60 mL of ethanol–HCl mixture solution (5 d 2 M HCl + 60 mL ethanol), centrifugally separated, washed three times with deionized water, and dried at 80 °C in a vacuum oven for 12 h. The obtained products were respectively labeled as CNTs@SiO₂ and CNTs-S@SiO₂.

2.3.2. Preparation of CNTs@SiO₂- and CNTs-S@SiO₂-compositesupported tungstophosphoric acid catalysts

NTs@SiO₂ and CNTs-S@SiO₂ (0.5 g) were dried at 100 °C in a vacuum oven overnight, and then treated them with given concentrations of tungstophosphoric acid solution (10%, 20%, 30%, and 40%) respectively by a procedure similar to that in Section 2.2 to get the final catalysts, named *w*%PW₁₂/CNTs@SiO₂ and *w*%PW₁₂/CNTs-S@SiO₂. The preparation procedures for the catalysts are shown in Scheme 1.

2.4. Baeyer-Villiger oxidation reaction of ketones

After 0.1 mmol ketone, 40 μ L 30% H₂O₂, and 3 mL of solvent were mixed in a 10-mL glass flask equipped with a reflux condenser, a given amount of catalyst was added. Then the reaction was carried out under microwave irradiation at a desired power for different times without stirring. The reaction products were analyzed by GC and GC/MS to evaluate the structures of the products, the conversion, and the selectivity.

For comparison, the catalytic reaction was also carried out at 80 °C using conventional oil-bath heating and magnetic stirring. It was found that conversion of cyclohexanone could reach 90% after 6 h with 30%PW₁₂/CNTs@SiO₂ or 30%PW₁₂/CNTs-S@SiO₂ as catalyst.



Fig. 2. Raman spectra of CNTs(a), CNTs-S (b), and 30%PW₁₂/CNTs-S(c).



Fig. 3. XPS survey spectrum of w%PW12/CNTs-S (A) and core-level spectra of C1s (B), W4f (C), and P2p (D) of 30%PW12/CNTs-S.

Table I												
Relationsh	p between	amounts (of surface	H_3PW_{12}	supported	on the	different	substrates	and th	neir catal	ytic a	ctivities.

Catalyst	Concentration of H_3PW_{12} (%)	XPS area ratio		XPS area ratio		W content by EDS (wt.%)	Conversion of cyclohexanone (%)	
		$A_{W4f}/A_{C=C}$	A_{W4f}/A_{Si2p}					
10%PW ₁₂ /CNTs-S	10	0.544		4.11	<10			
20%PW12/CNTs-S	20	0.649		9.83	65			
30%PW12/CNTs-S	30	0.859		15.31	94			
10%PW12/CNTs-S@SiO2	10		0.954	15.13	<10			
20%PW12/CNTs-S@SiO2	20		1.01	29.19	73			
30%PW12/CNTs-S@SiO2	30		1.10	34.21	90			

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. FT-IR spectra of the catalysts

Fig. 1 shows IR spectra of the samples. IR spectra of CNTs (Fig. 1A(a)) and CNTs-S (Fig. 1A(b)) were very similar. –OH and adsorbed H₂O stretching vibrations appeared near 3420 cm⁻¹. The absorption band at 1543 cm⁻¹ was assigned to the E_{1u} vibration mode, indicating the existence of a graphite structure of CNT walls [17]. At 2360 cm⁻¹ was the absorption peak of CO₂ in the environment. The band at 1630 cm⁻¹ resulted from the C=C stretching vibration of five-member rings or seven-member rings at the bend and sealing of CNTs [18]. However, when CNTs were oxidized, these peaks disappeared, suggesting that CNTs had been cut off, which was advantageous to guest transfer. In addition, the IR spectra of CNTs-S showed a weak, but well-defined C=O band near 1700 cm⁻¹, which was assigned to aldehyde or carboxyl.

Because we used the gas oxidation method with HNO₃ as sole oxidant, the oxidation degree was low and the content of the obtained surface functional groups, especially carboxyl, was relatively low. Some weak peaks at 2900–3000 cm⁻¹ indicated the existence of alkyl groups. When H_3PW_{12} was supported on CNTs-S, all of the characterization peaks of the H_3PW_{12} Keggin structure appeared. The symmetrical stretching vibration of the PO₄ tetrahedron was located at 1072 cm⁻¹, the asymmetrical stretching vibration of the W=O_d bond at 980 cm⁻¹, the asymmetrical stretching vibration of the W-O_b-W bond linked with the corner-sharing oxygen bridge 887 cm⁻¹, and the asymmetrical stretching vibration of the W-O_c-W bond linked with the edge-sharing oxygen bridge at 795 cm⁻¹.

When the surfaces of CNTs-S were coated with SiO₂ (Fig. 1B), —OH stretching vibration peaks from adsorbed water, silanol groups, and tungstophosphoric acid appeared near 3410 cm^{-1} , and related bend vibrations at 1640 cm^{-1} . The strong peak at 1088 cm^{-1} was assigned to asymmetrical stretching vibration of



Fig. 4. XPS survey spectra of w%PW12/CNTs-S@SiO2 (A) and core-level spectra of C1s (B), Si2p (C), P2p (D), and W4f (E) of 30%PW12/CNTs-S@SiO2.

the Si–O–Si bond, the peak at 801 cm⁻¹ was its symmetrical mode, and the peak at 463 cm⁻¹ was its bend vibration. These results indicated that the materials had been coated successfully. In IR spectra of 30%PW₁₂/CNTs-S@SiO₂, all of the characterization peaks of tungstophosphoric acid appeared and their intensities were very high, indicating that a high content of tungstophosphoric acid was supported on the CNTs-S@SiO₂ substrate.

3.1.2. Raman spectra of CNTs-S and 30%PW₁₂/CNTs-S

Fig. 2 shows Raman spectra of CNTs (a), CNTs-S (b), and 30% $PW_{12}/CNTs$ -S (c). The D band and G band of CNTs were respectively located at 1348.4 and 1594.6 cm⁻¹ and I_D/I_G = 1.285. When CNTs were oxidized as CNTs-S, the intensity ratio of the D band at 1351.5 cm⁻¹ and the G band at 1586.8 cm⁻¹ increased to 1.643, indicating that defects and disorder increased. But when tungstophosphoric acid was supported, the ratio decreased slightly



Fig. 5. TG curves of CNTs (a), CNTS-S (b), $30\% PW_{12}/CNTs$ -S (c), and $30\% PW_{12}/CNTs$ -S@SiO_2 (d).



Fig. 6. N_2 adsorption and desorption isotherms of $30\% PW_{12}/CNTs\text{-S}$ and $30\% PW_{12}/CNTs\text{-S}@SiO_2.$

to 1.564. Further observation showed that the intensities of the D band and G band of CNTs-S were obviously higher than those of their parent CNTs and the G band red-shifted 7.8 cm⁻¹, suggesting that the length-diameter ratio and tube length were decreased [19]; that is, CNTs had been successfully cut off after oxidation.

3.1.3. XPS analysis of the catalysts

Fig. 3 shows The XPS survey spectrum of CNTs-S with different loading amounts of tungstophosphoric acid and high-resolution elemental scans of C1s, W4f, and P2p of 30%PW₁₂/CNTs-S. Fig. 3A shows that the catalyst contains C, O, and W elements. The C1s core-level spectrum included four components with BEs at 284.37, 284.94, 285.77, and 288.33 eV (Fig. 3B), attributable to C=C, C-C, C-O/C=O, and COOH, respectively. According to the

peak area, carbon from carboxyl was only 7.4% of total carbon, which indicated that the HNO₃ gas-phase oxidation employed here produced only a small number of carboxyl groups, so that the surface of the resulting CNTs-S was relatively hydrophobic and favorable to assembly of the surfactant molecules. In addition, at 134.81 eV appeared a P2*p* peak, and at 36.0 eV and 38.13 eV respectively appeared strong W4*f*_{7/2} and W4*f*₅/2 spin–orbit coupling peaks. These results were very strong evidence of tungstophosphoric acid support.

With increasing concentration of the tungstophosphoric acid dipping solution (10, 20, and 30 wt%), the $A_{W4f}/A_{C=C}$ area ratio gradually increased (0.544, 0.649, 0.859), indicating that the surface loading amounts of tungstophosphoric acid increased successively, which was consistent with EDS results (Table 1).

Fig. 4 shows the survey spectrum of W PW₁₂/CNTs-S@SiO₂ and the core-level spectra of C1s, Si2p, P2p, and W4fs. The C1s spectrum was in accordance with CNTs-S as mentioned above. Si2s and Si2p BEs were respectively located at 158.4 and 103.86 eV, assigned to Si⁴⁺–O. P2p BE at 134.50 eV and W4f_{7/2} and W4f_{5/2} BEs at 36.36 and 38.36 eV were respectively attributable to P⁵⁺–O and W⁶⁺–O. As the concentration of the tungstophosphoric acid solution increased from 10 to 20 and 30 wt%, the A_{W4f} / A_{Si2p} area ratio increased from 0.964 to 1.01 and 1.10, which accorded with EDS results (Table 1).

3.1.4. Thermal stability of the catalysts

Fig. 5 is the TG curves of the samples. CNTs(a) hardly had any weight loss below 730 °C. CNTs-S(b) was stable below 220 °C, but had a continuous weight loss process from 220 to 730 °C with a weightlessness rate of ~ 8%, attributed to removal of substituent groups on CNTs-S. After 730 °C, the CNTs-S skeleton started to decompose. These results indicated that the CNTs-S skeleton was sufficiently stable. CNTs-S-supported catalyst (c) had about 4% weight loss below 170 °C, attributed to removal of adsorbed water,



Fig. 7. SEM images of CNTs (A), CNTs-S (B), and CNTs-S@SiO₂ (C).



Fig. 8. TEM images of CNTs (A, B), CNTs-S (C, D), and CNTs-S@SiO₂ (E, F).

and two small weight loss ranges between 200 and 730 °C, corresponding to decomposition of organic groups on CNTs-S and removal of partial structural water of tungstophosphoric acid. In the TG curve of SiO₂-coated CNTs-S-supported catalyst (d), the weight loss process below 350 °C resulted from removal of adsorbed water and silica gel dehydration, and after that, it would successively experience residual template removal, hydrous silica and tungstophosphoric acid structural water removal, and CNTs-S structure decomposition. Overall, CNTs-S- and CNTs-S@SiO₂supported catalysts basically remained stable below 500 °C and displayed sufficient thermal stability.

3.1.5. N₂ Adsorption–desorption isotherms of the catalysts

Fig. 6 is the N₂ adsorption–desorption isotherms of $30\% PW_{12}/CNTs-S$ and $30\% PW_{12}/CNTs-S@SiO_2$. It could be seen that these two isotherms were very similar and corresponded to type IV with an obvious hysteresis loop. The BET surface areas were calculated to be 164.2420 and 203.8966 m²/g, and the BJH pore volumes were 1.026232 and 0.595129 cm³/g, respectively. The isotherm of 30% PW₁₂/CNTs-S@SiO₂ still showed a sharp uptake below $P/P_0 = 1.0$, indicating the existence of mesopores and macropores.

3.1.6. Surface morphologies of the catalysts

Fig. 7 is SEM images of CNTs (A), CNTs-S (B), and CNTs-S@SiO₂ (C). Purified CNTs were very pure and possessed a very smooth surface and a higher length-diameter ratio (A). After CNTs oxidation, the diameter became greater and the surface was rougher. At the same time, many breaches appeared on the wall and some tubes got shorter. These characteristics made them very advantageous for diffusion and transfer of the quest molecules when they were used as a catalyst matrix. When CNTs-S was coated with SiO₂ the diameter became larger and better distributed.

Fig. 8 is TEM morphology images of CNTs (A, B), CNTs-S (C, D), and CNTs-S@SiO₂ (E, F). The diameter of CNTs was about 20 nm; after oxidation, it became 25 nm, and breaches were observed. When coated with SiO₂, the composite tube had an outer diameter of some 100 nm and an inner diameter of some 50 nm, and CNTs-S was distinctly enveloped in an SiO₂ nanotube to form a hierarchical structure. The designed purpose had been achieved.

Fig. 9 displays the morphologies of CNTs-S- and CNTs-S@SiO₂supported catalysts. The catalytic active component tungstophosphoric acid was well dispersed on the inner and outer surfaces of CNTs-S and CNTs-S@SiO₂. This structure was very favorable to contact of the reactant molecules with the active sites of the catalyst.



Fig. 9. Morphologies of the prepared catalysts: (A, B) SEM and TEM images of 30%PW₁₂/CNTs-S; (C, D) SEM and TEM images of 30%PW/CNTs-S@SiO₂.

3.2. Catalytic activities of the catalysts for Baeyer–Villiger oxidation of cyclic ketones

3.2.1. Optimization of the reaction conditions

In this paper, catalytic activities of the prepared catalysts for Baeyer–Villiger oxidation of cyclic ketones with H_2O_2 as oxidant under microwave irradiation were investigated. First, the experimental conditions were optimized and the results are listed in Table 2.

From Table 2, it can be found that B-V oxidation of cyclohexanone did not happen without catalyst or oxidant. While 30% $PW_{12}/CNTs$ -S and $30\% PW_{12}/CNTs$ -S@SiO₂ displayed excellent catalytic performance, the conversion was comparable to that of the homogeneous catalyst $H_3 PW_{12}$ and reached 94% and 90%, respectively.

CNTs, CNTs-S, and the corresponding SiO₂-coated products CNTs@SiO₂ and CNTs-S@SiO₂ did not show any catalytic properties. But when tungstophosphoric acid was supported, all of the catalysts displayed catalytic abilities to a certain extent, indicating that tungstophosphoric acid was the catalytically active component. w% PW₁₂/CNTs-S had higher activity than *w*%PW₁₂/CNTs, which was because more catalytically active components could enter CNTs through sieve pores distributed on the inner and outer surfaces of the walls and sufficiently contacted with freely entered reactant molecules, whereas in CNTs the substrate molecules could only enter through the terminal opening, which limited free diffusion of the substrate molecules. For the same reason, the catalytic activity of w%PW₁₂/CNTs-S@SiO₂ was higher than that of w%PW₁₂/ CNTs@SiO₂. The results also showed that the obtained catalysts 30%PW₁₂/CNTs-S and 30%PW₁₂/CNTs-S@SiO₂ in 30 wt% dipping solution had the highest catalytic activity in the same series of catalysts.

w%PW₁₂/CNTs-S serial catalysts possessed higher catalytic activity than w%PW₁₂/CNTs-S@SiO₂ serial catalysts. This was

because SiO₂ coating decreased the freedom of the substrate molecules and prevented them from entering CNTs and contacting active sites. However, due to a relatively high surface loading H₃PW₁₂ amount and large specific surface area, w%PW₁₂/CNTs-S@SiO₂ still maintained satisfactory catalytic activity; for example, 30%PW₁₂/CNTs-S@SiO₂ showed 90% conversion.

GC–MS analysis results of the products of cyclohexanone conversion indicated that the byproduct was 6-hydroxycaproic acid, suggesting that produced ε -caprolactone was continually hydrolyzed to acid (Scheme 2).

This mechanism is possibly relevant to the strong acidity of H_3PW_{12} . It ensures high catalytic activity of the catalyst, on one hand; on the other hand, it enhances the hydrolysis efficiency of the product to decrease the lactone selectivity. From Table 2, we could find that with increasing reaction time, conversion of cyclohexanone increased, but lactone selectivity decreased and degree of hydrolysis of the lactone increased.

Solvent types had also a remarkable effect on the catalytic activity of the catalysts. 1, 2-Dichloroethane was the best solvent for the B-V reaction of cyclohexanone. In this solvent, $30\%PW_{12}/CNTs-S$ and $30\%PW_{12}/CNTs-S@SiO_2$ possessed the highest conversion, 94% and 90%. Ethanol was the best protic solvent, providing 62% conversion. Unfortunately, other solvents did not show acceptable conversion, especially in CH₃CN and DMF, where the reaction could not occur. In different solvents, the activity order of the catalysts was dichloroethane > EtOH > CCl_4 > hexane > dioxane > CH_3-CN ~ DMF. The roles of different solvents in the catalytic reaction still need to be studied further.

From Table 2, the optimal experimental conditions were selected as 10 mg of catalyst dosage, medium irradiation power (400 W), 5 min of reaction time, 40 μ L of 30 wt% H₂O₂ dosage, and 1, 2-dichloroethane as solvent.

To evaluate completely the application performance of the prepared catalysts, a comparison of the catalysts with those reported

Table 2

Catalytic performance of the prepared catalysts and optimization of the experimental conditions for B-V oxidation of cyclohexanone by H₂O₂.^a

Catalyst H_2O_2 dosage (µL)Solvent T (min)Conversion	on (%) ^b Selectivity (%) ^b
Type Added (mg) Type ^c Added (mL)	
40 DCE 3 5 0	0
H ₃ [PW ₁₂ O ₄₀]·xH ₂ O 10 0 DCE 3 5 0	0
H ₃ [PW ₁₂ O ₄₀]·xH ₂ O 10 40 DCE 3 5 91	77
30%PW ₁₂ /CNTs-S 10 0 DCE 3 5 0	0
30%PW ₁₂ /CNTs-S 10 40 DCE 3 5 94	75
30%PW ₁₂ /CNTs-S@SiO ₂ 10 0 DCE 3 5 0	0
30%PW ₁₂ /CNTs-S@SiO ₂ 10 40 DCE 3 5 90	75
MWCNTs ^d 10 40 DCE 3 5 0	0
CNTs 10 40 DCE 3 5 0	0
CNTs-S 10 40 DCE 3 5 0	0
CNTs@ SiO ₂ 10 40 DCE 3 5 0	0
CNTs-S@ SiO ₂ 10 40 DCE 3 5 0	0
10%PW ₁₂ /CNTs 10 40 DCE 3 5 <10	_
20%PW ₁₂ /CNTs 10 40 DCE 3 5 57	76
30%PW ₁₂ /CNTs 10 40 DCE 3 5 72	70
40%PW ₁₂ /CNTs 10 40 DCE 3 5 47	72
10%PW ₁₂ /CNTs-S 10 40 DCE 3 5 <10	_
20%PW ₁₂ /CNTs-S 10 40 DCE‡ 3 5 65	70
30%PW ₁₂ /CNTs-S 10 40 DCE 3 5 94	75
40%PW ₁₂ /CNTs-S 10 40 DCE 3 5 68	73
10%PW ₁₂ /CNTs@SiO ₂ 10 40 DCE 3 5 <10	_
20%PW ₁₂ /CNTs@ SiO ₂ 10 40 DCE 3 5 57	73
30%PW ₁₂ /CNTs@SiO ₂ 10 40 DCE 3 5 78	68
40%PW ₁₂ /CNTs@ SiO ₂ 10 40 DCE 3 5 34	76
10%PW ₁₂ /CNTs-S@SiO ₂ 10 40 DCE 3 5 <10	_
20%PW ₁₂ /CNTs-S@SiO ₂ 10 40 DCE 3 5 73	78
30%PW ₁₂ /CNTs-S@SiO ₂ 10 40 DCE 3 5 90	75
40%PW ₁₂ /CNTs-S@SiO ₂ 10 40 DCE 3 5 52	77
30%PW ₁₂ /CNTs-S 10 40 CCl ₄ 3 5 31	49
30%PW ₁₂ /CNTs-S 10 40 hexane 3 5 26	58
30%PW ₁₂ /CNTs-S 10 40 CH ₃ CN 3 5 0	_
30%PW ₁₂ /CNTs-S 10 40 DMF 3 5 0	_
30%PW ₁₂ /CNTs-S 10 40 Diox 3 5 15	34
30%PW ₁₂ /CNTs-S 10 40 EtOH 3 5 62	20
30%PW ₁₂ /CNTs-S 3 40 DCE 3 5 56	74
30%PW ₁₂ /CNTs-S 5 40 DCE 3 5 79	71
30%PW ₁₂ /CNTs-S 10 40 DCE 3 5 94	75
30%PW ₁₂ /CNTs-S 15 40 DCE 3 5 95	87
30%PW ₁₂ /CNTs-S 10 40 DCE 3 1 <10	88
30%PW ₁₂ /CNTs-S 10 40 DCE 3 2 15	76
30%PW ₁₂ /CNTs-S 10 40 DCE 3 3 37	75
30%PW ₁₂ /CNTs-S 10 40 DCE 3 4 84	78
30%PW ₁₂ /CNTs-S 10 40 DCE 3 5 94	75
30%PW ₁₂ /CNTs-S 10 40 DCE 3 6 93	82

^a Cyclohexanone amount: 0.1 mmol; microwave power: 400 W.

^b Conversion and selectivity measured by GC.

^c DCE: dichloroethane; Diox: dioxane.

^d MWCNTs: commercially available multiwalled carbon nanotubes.



Scheme 2. Reaction pathway of BV oxidation of cyclohexanone.

recently was also made and the results are given in Table 3. It was found that our prepared catalysts had comparable or even better performance, indicating that they had a good application potential.

3.2.2. Catalytic behavior of 30%PW12/CNTs-S for other cyclic ketone B-V reactions

For investigating applicability of the prepared catalysts, their catalytic behavior for other ketone B-V reactions were also studied and typical results were tabulated in Table 4.

From Table 4, it was found that the catalyst 30%PW₁₂/CNTs-S had catalytic activity for B-V oxidation of almost all cyclic ketones except for 2-*tert*-butyl cyclohexanone, in which high steric hindrance of *ortho-tert*-butyl of carbonyl limited the occurrence of the reaction. In addition, the catalyst did not show any catalytic activity for B-V reactions of chain ketones; the reason was not clear. However, the behavior suggested that the catalysts had good selectivity for cyclic ketones.

It is noteworthy that cyclobutanone, cyclopentanone, and adamantane displayed nearly quantitative conversion, and lactone

Table 3

Comparison of the prepared catalysts with those reported recently.

Catalysts	Reaction conditions	Cyclohexanone conversion (%)	Selectivity (%)	Ref.
H-type β-zeolite (Si/Al = 39)	30% H ₂ O ₂ , acetonitrile, 30 °C, 3 h	48	52	[20]
Re complexes	1, 2-dichloroethane, 30% H ₂ O ₂ , 70 °C, 6 h	24–57	5-69	[21]
H ₄ O ₄₀ SiW ₁₂ /SBA-15	30% H ₂ O ₂ , 1, 2-dichloroethane, 70 °C, 8 h	86	99	[22]
Sn-Beta-HT	1, 4-dioxane, 30% H ₂ O ₂ , 80 °C, 3 h	30	62	[23]
Ag/WO ₃	H ₂ O ₂ , acetonitrile, 80 °C, 9 h	97	99	[24]
MgO/SnO ₂ /WO ₃	50% H ₂ O ₂ + acetic acid, 50 °C, 3 h	86	94	[25]
Mg–Al hydrotalcite-like materials	30% H ₂ O ₂ , acetonitrile, 70 °C, 6 h	30-40	70-100	[26]
30%PW12/CNTs-S	1, 2-dichloroethane, 30% H ₂ O ₂ , MW, 5 min	94	75	This work
30%PW12/CNTs-S@ SiO2	1, 2-dichloroethane, 30% H ₂ O ₂ , MW, 5 min	90	75	

Table 4

B-V oxidation of ketones catalyzed by $30\% PW_{12}/CNTs$ -S.^a

Substrate	Conversion (%)	Selectivity (%)	Product
 0	94	75	0
			\bigvee
0 	99	>99	
			<u> </u>
0	98	>99	O II
\bigwedge			C o
	22		\bigvee
	98	>99	
			400
ů. O	86	25	Ŷ
CH ₃			r o
			CH3
0	98	46	0
\mathbf{Y}			\rightarrow
ĊH₃ O	0	0	H ₃ C
C(CH ₃) ₃	0	0	1
) 0=	96	32	O II
			<u> </u>
\bigvee			\searrow
C(CH ₃) ₃	C2	54	(H ₃ C) ₃ C
	03	54	
			∽⊂сн₃
	0	0	1
	0	0	1
ČCH–CH2–Č–CH2–CH			

^a Conditions: 0.1 mmol ketone, 10 mg catalyst, 3 mL DCE, 5 min irradiation. Conversion and selectivity were measured by GC.

selectivity reached 100%. This is within expectation because fivemembered and six-membered rings, as we know, have the smallest ring tension and the highest stability among cyclic compounds. Due to the special polycyclic structure of adamantane lactone, its stability is also high enough. High stability avoids subsequent hydrolysis of lactone products.

3.3. Cycle life of the catalysts

Cycle performance of two kinds of catalysts was studied with cyclohexanone as a model substrate. Used catalysts were centrifugally separated, dried, and then directly used in the next cycle. The results are shown in Fig. 10.



Fig. 10. Cycle performances of the catalysts $30\%PW_{12}/CNTs-S$ and $30\%PW_{12}/CNTs-S@SiO_2$ in catalyzing B-V oxidation of cyclohexanone. Conditions: 0.1 mmol ketone, 10 mg catalyst, 3 mL 1,2-dichloroethane, 5 min irradiation. Conversion and selectivity were measured by GC.

In the first three cycles, $30\%PW_{12}/CNTs$ -S exhibited higher catalytic activity than SiO₂-coated catalyst, but the conversion decreased rapidly afterward. In the tenth cycle, it was lower than half of the initial value. In contrast, $30\%PW_{12}/CNTs$ -S@SiO₂ displayed higher cyclic stability and in the tenth cycle, the conversion still was nearly 80%, decreased only by 12.2%. The results showed that SiO₂ coating effectively reduced loss of the catalyst.

4. Conclusions

Carbon-nanotube-sieve-supported tungstophosphoric acid and SiO₂-coated-carbon nanotube-sieve-supported tungstophosphoric acid with dual pore structure were successfully prepared. These two catalysts showed excellent catalytic activities for Baeyer-Villiger oxidation of cyclic ketones with hydrogen peroxide as oxidant. Cyclopentanone and adamantanone approached quantitative conversion, and lactone selectivity reached 100%. SiO₂ coating effectively reduced loss of the catalytically active component and ensured long cycle life. The proposed preparation method provided a new and general strategy for designing and fabricating Baeyer-Villiger oxidation reaction catalysts. In addition, with microwave irradiation instead of traditional oil bath heating, the reaction time dramatically decreased from several hours to several minutes, which manifested favorable green and energy-saving characteristics.

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