Tungsten doped mesoporous SBA-16 as novel heterogeneous catalysts for oxidation of cyclopentene to glutaric acid

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Natural Research Major Foundation of Shan Dong Province, Grant/Award Number: ZR2017ZC0632; National Natural Science Foundation of China, Grant/Award Number: NSFC21376128 Novel heterogeneous tungsten species in mesoporous silica SBA-16 catalysts based on ship-in-a-bottle methodology are originally reported for oxidizing cyclopentene (CPE) to glutaric acid (GAC) using hydrogen peroxide (H₂O₂). For all W-SBA-16 catalysts, isolated tungsten species and octahedrally coordinated tungsten oxide species are observed while WO₃ crystallites are detected for the W-SBA-16 catalysts with Si/ W = 5, 10, and 20. The specific surface areas and the corresponding total pore volumes decrease significantly as increasing amounts of tungsten incorporated into the pores of SBA-16. Using tungsten-substituted mesoporous SBA-16 heterogeneous catalysts, high yield of GAC (55%) is achieved with low tungsten loading (for Si/W = 30, ~13 wt%) for oxidation of CPE. The W-SBA-16 catalysts with Si/W = 30 can be reused five times without dramatic deactivation. In fact, low catalytic activity provided by bulk WO₃ implies that the highly distributed tungsten species in SBA-16 and the steric confinement effect of SBA-16 are key elements for the outstanding catalytic performance.

KEYWORDS

cyclopentene, glutaric acid, heterogeneous catalysis, supported catalysts, W-SBA-16

1 | INTRODUCTION

Glutaric acid (GAC, dicarboxylic acid) has many compelling physicochemical properties. One of the most important applications of GAC and its derivatives is used for the synthesis of liquid crystal materials (e.g., liquid crystal displays).^[1] GAC is an essential feedstock for the synthesis of lubricating oil, polyester, synthetic rubber, and polyamide.^[2] It has also been reported in medicine that GAC displays important physiological activity to reduce glutamate uptake,^[3] inhibit the energy metabolism,^[4] and induce oxidative stress in brain.^[5] Several procedures for synthesis of GAC have been described using trimethylene cyanide,^[6] methylene bis(malonic acid),^[7] and γ -butyrolactone.^[8] However, these methods are inconvenient and unsuitable for large-scale synthesis. Amino acids,^[9] alkanes,^[10] ketones,^[11,12] alcohols,^[13] and 1,3-dicarbonyl derivatives^[14] have also been reported to manufacture carboxylic acids, but they are rarely used or required complicated multi-step to fabricate GAC. Phase-transfer catalysts W/[CH₃(n-C₈H₁₇)₃N]HSO₄ and $[\pi$ -C₅H₅NC₁₆H₃₃]₃[PW₄O₁₆] have been proposed for selective oxidation of olefins using H_2O_2 by Noyori *et al.*^[15] and Sun et al.,^[16] repectively. However, the low recovery rate of the phase-transfer catalysts and the irreversible structure of catalysts change after the reaction limit their application. H₂WO₄ has also been used as a homogeneous catalyst for oxidation of cyclopentene (CPE) to GAC, but it is also difficult to recover.^[17] A green synthesis route for oxidizing reaction of CPE to GAC has been suggested,^[18] the catalyst needs to be further explored. Vafaeezadeh et al.^[19] have put forward the use of bis (1-butyl-3-methylimidazolium) tungstate for the prepare of GAC through oxidative cleavage of CPE. A desired yield of GAC can be obtained when ptoluenesulfonic acid or trifluoromethanesulfonic acid was selected to provide acidic media. WO₃/SiO₂ synthesized by ultrasound impregnation method has also been used to catalyze the oxidation of CPE.^[20] Heterogeneous catalysts show distinct advantages for catalyst recovery over homogeneous and phase-transfer catalysts; heterogenization of homogeneous catalysts has become an important research direction.

Different approaches, such as chemical grafting,^[21,22] encapsulating in porous supports (ship-in-a-bottle),^[23,24] using organic and inorganic hybrids,^[25,26] intercalating lavered materials,^[27,28] and forming ionic interactions,^[29,30] have been suggested to create heterogeneous catalysts. The ship-in-a-bottle method maintains the chemical characteristics of the doped catalyst but not the steric confinement of the multi-hole carriers. It is a valid method to imitate homogeneous catalysts. Sulikowski et al.^[31] proposed the ship-in-a-bottle method and successfully packaged phosphotungstic acid in the cage of a Y zeolite; the encapsulated catalyst could be easily recovered for reuse. However, the zeolite is only applicable for small-molecule reactions because of its pore size (<1 nm). This makes it necessary to seek new materials with larger pores to accelerate the appearance of ordered mesoporous silicas (OMSs).

OMSs initiated by Kresge et al.^[32] have wide applications in many domains, such as catalysis,^[33] separations,^[34] and adsorption,^[35] because of their superior and adjustable specific surface areas, mesopore volumes, and pore diameters. A tungsten complex, which is an efficient catalyst for the oxidation of olefins, was immobilized on silica to form metal-incorporated mesoporous materials. Different mesoporous silica materials (e.g., MCM-41, MCM-48, HMS, SBA-15, and KIT-6) have been examined for catalytic applications. W-MCM-41 was synthesized, and its textural and structural properties were probed.^[36] Fan *et al.*^[37–39] doped tungsten inside the pores of ordered MCM-48, HMS, and SBA-15, which exhibited high selectivity for the oxidation of CPE to glutaric dialdehyde. Tungsten-modified SBA-15 and HMS were also detected as carriers for Ni/W catalysts in the highly dispersible silica reaction of thiophene by the Jiratova group.^[40] Zhou et al.^[41] triumphantly immobilized tungsten into KIT-6 under hydrothermal conditions. Nevertheless, 3D mesoporous SBA-16 has not attracted much attention. SBA-16 is a well-ordered porous silica with large cage-like mesopores arranged in a cubic body-centered Im^{-3m} symmetry,^[42] in which adjacent cages form a polydirectional system of mesoporous reticulation via eight small pores; this structure facilitates mass transfer without blocking the pores. The distinct structure of SBA-16 is undoubtedly beneficial to improve the activity of tungsten catalysts. Nevertheless,

the oxidation of CPE to GAC has not been catalyzed by tungsten-doped cage-type mesoporous silica SBA-16 heterogeneous catalysts.

Here, we first reported tungsten doped into the cages of SBA-16 catalysts for the oxidation of CPE to GAC and compared the catalytic performance of tungsten doped SBA-16 catalysts with different tungsten loading. Physicochemical properties of the synthesized catalysts using one-pot method^[43] were characterized by X-ray diffraction (XRD), N₂ adsorption-desorption analysis, diffuse-reflectance ultraviolet-visible light (DR-UV-Vis) microscopy, fourier transform infrared spectroscopy (FT-IR), temperature programmed reduction for hydrogen (H₂-TPR), and temperature programmed desorption of ammonia (NH₃-TPD). This research produces an effective and returnable catalyst for direct oxidation of CPE to GAC and certifies the outstanding capacity of SBA-16 as an extremely efficient catalyst support.

2 | EXPERIMENTAL

2.1 | Encapsulation of tungsten in the nanocage of SBA-16

Mesoporous W-SBA-16 catalysts were synthesized according to a literature procedure with some adaptations:^[44,45] the samples are named based on their Si/W mole ratio (i.e., W-SBA-16 (Si/W)). Typically, Triblock copolymer Pluronic F127 (3.5 g, EO₁₀₆PO₇₀EO₁₀₆, Macklin) was dissolved in a HCl solution (175 ml, 0.4 M) at 45 °C with vigorous stirring for 20 min. Then, *n*-butanol (10.5 g, Aladdin) was added and continuously stirred for 1 h. Tetraethyl orthosilicate (16.7 g, Macklin) and moderate amounts of sodium tungstate (Aladdin) were added and continuously stirred for 24 h. The resulting reaction mixture was treated at 100°C for 24 h under an idle state in a hydrothermal synthesis reactor. After filtration, a white solid product was obtained. Then, the product was dried at 100 °C for 12 h and calcined at 550 °C (temperature increase of 1 °C/min) for 6 h under air flow to remove the template.

2.2 | Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rint 2000 vertical goniometer (Rigaku) equipped with Cu K α radiation ($\lambda = 0.15418$ nm) and operated at 40 kV and 100 mA with a scanning speed of 2°(2 θ)/min. N₂ adsorption isotherms were measured at -196 °C on an ASAP 2020 V4.01 (V 4.01 H; Micromeritics) sorptometer. Before the physisorption measurement, all samples were outgassed at 150 °C for 2 h. Diffuse reflectance UV-Vis (DR UV-Vis) spectra were measured using a Cary 500 (8.01) spectrophotometer from 200-800 nm at 25 °C. Fourier transform infrared (FT-IR) spectra were recorded on a HGCS20170343J spectrometer from 1400-400 cm⁻¹ using the KBr pellet technique. Temperatureprogrammed reduction (H₂-TPR) was performed using a Micromeritics AutoChem II 2920 V 4.03 apparatus. Temperature programmed desorption of ammonia (NH₃-TPD) was recorded on Chembet Pulsar TPR/TPD instrument. Typically, 100 mg sample was pretreated in He (30 ml/min, 400 °C, 1 h). Subsequently, the sample was exposed to 10%NH₃/90% He at 80 °C for 1 h, then purged with He for 0.5 h at 100 °C. The spectra of NH₃-TPD were registered from 100 to 500 °C with a ramp of 10 °C/min. The tungsten contents in W-SBA-16 and the reaction liquids were measured by inductively coupled plasmaoptical emission spectrometry (ICP-OES, IRIS Intrepid, Thermo Elemental Company) after solubilization of W-SBA-16 in HF (40 wt% in water)/HNO₃ (65 wt% in water) solutions in which the volume ratio of HF to HNO₃ is 3:7. Liquid chromatography (LC, Agilent 1100) was carried out using a Microsorb-MV C18 (4.6 mm × 250 mm) analytical column with aqueous methanol (0.1-0.3 volume fraction) and aqueous KH₂PO₄ (5 mmol/l) as the mobile phase with a flow rate of 1 ml/min. Gas chromatography (GC, GC-1102, Shanghai Analytical Instrument Factory) was carried out using an SE-30-filled stainless steel packed column (Φ 3 mm \times 2 m).

2.3 | Oxidation of CPE

A three-neck round bottomed flask (25 ml), condensation tube, balloon, and thermometer were used in this experiment. The reaction process was violently exothermic; therefore, a temperature-controlled water bath was used to easily control the temperature. An appropriate amount of the catalyst (based on the tungsten content), H_2O_2 (50 wt%, 2.99 g), and CPE (0.68 g) were blended into the flask. The mixture was heated at 50 °C with vigorous stirring. CPE began to reflux when the temperature reached 45 °C. The temperature was set to 90 °C and maintained for ~7 h until the reflux was complete.^[46] The resulting suspension was filtered to obtain the catalysts and a colorless liquid (a colored liquid was obtained when WO₃ was used as the catalyst). The colorless liquid was divided into four portions. One portion was titrated using NaOH (0.487 mol/l) liquor to obtain the yield of organic acid. Similarly, KMnO₄ (0.005 mol/l) liquor was required to titrate a second portion to determine the residual content of H_2O_2 . The third portion reacted for another 7 h at 90 °C. Then, the yield of organic acid and residual H_2O_2 content were re-tested. The fourth portion was boiled to disintegrate residual H₂O₂ under vacuum distillation to avoid explosion. This process was repeated several times until the solution became red from titration with trace $KMnO_4$ (0.005 mol/l) liquor. Then, it was concentrated through vacuum distillation to remove part of the water, refrigerated at 0 °C for 5 h, and filtered to form the colorless GAC crystal.

LC and GC were used to analyze the purity of GAC. Quantitative analysis by GC: A BF₃-ether solution (1 ml) was added to absolute ethanol (5 ml) containing 0.1 g of the solid sample. The mixture was esterified under sealed conditions at 100 °C for 10 min. A solution of NaHCO₃ and deionized water were added to the cooled esterification reaction liquid to neutralize it and dissolve inorganic substances, respectively. Then, the neutral solution was extracted three times with anhydrous ether (3 ml), and diethyl malonate (0.1 g) was added to the ether extract to obtain an injection solution.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

The mesoporosity of the W-SBA-16 catalysts were examined using small-angle XRD measurement, and the corresponding results are described in Figure 1. A wellresolved diffraction peak of the (110) reflection (2 θ = 0.84°), a small shoulder of the (200) reflection (2 θ = 1.01°), and another small shoulder of the (211) reflection (2 θ = 1.25°) assigned to the cubic *Im*^{-3m} structure are observed in SBA-16.^[45,47] The three diffraction peaks are also detected in the W-SBA-16 catalysts; it indicates the mesoporous structures still maintain after the immobilization of tungsten species. The strength of the (110), (200), and (211) reflection peaks gradually decreases in W-SBA-16 catalysts with increasing amounts of tungsten. When Si/W \leq 20, the intensity of the (110) reflection peak



FIGURE 1 Small-angle XRD patterns of SBA-16 and W-SBA-16 catalysts

decreases significantly and the characteristic peaks ascribed to (200) and (211) reflection become less obvious; those results suggest the long-range ordering of the mesoporous structure is destroyed partially. Furthermore, the peak attributed to (110) in W-SBA-16(20, 10, and 5) is broader than that in W-SBA-16(50, 40, and 30). It also suggests partial disruption of the structural ordering at Si/W \leq 20. As inferred from Table 1, the tungsten contents measured in the W-SBA-16 catalysts from ICP test are practically similar to the theoretical values with an experimental error of a little bit less than 7 wt% for W-SBA-16(10) and W-SBA-16(5) samples; this result indicates that some tungsten is successfully incorporated inside the SBA-16.

Wide-angle XRD images of SBA-16 and the W-SBA-16 catalysts are shown in Figure 2. The characteristic diffractions of mesoporous silica ($2 \theta = 15^{\circ}-30^{\circ}$) are detected for all the samples.^[44] No bulk WO₃ peaks are observed for the W-SBA-16 catalysts with tungsten loadings \leq 12.99 wt% (W-SBA-16(30)) (Table 1). WO₃ crystal phase characteristic reflections are not detected in the W-SBA-16(30, 40, and 50) catalysts suggesting the presence of highly dispersed tungsten species in SBA-16.^[44] However, in W-SBA-16(5, 10, and 20) catalysts, characteristic peaks corresponding to bulk WO₃ are clearly observed and their intensities increase with the increase of tungsten content.

The textural properties of all the samples are shown in Figure 3. All samples reveal type-IV isotherms with an H2-type hysteresis loop indicating typical cage-like porous structures according to the IUPAC classification.^[45,48] The sharp capillary condensation step of N₂ (when P/P₀ = 0.4-0.8) indicates the uniform hole size of all samples. For the W-SBA-16 materials, inflection is less sharp than that of SBA-16 and attenuated with increasing W content. This phenomenon signifies the decrease of framework mesoporosity. From Table 1, the value of BET surface area



FIGURE 2 Wide-angle XRD patterns of SBA-16 and W-SBA-16 catalysts

 (S_{BET}) drastically decreases from 672 (W-SBA-16(50)) to 330 m²/g (W-SBA-16(5)); meanwhile a gradual decline of the corresponding total pore volume (V_{tot}) is observed from 0.61 to 0.34 cm^3/g . The differences are caused by the different amount of tungsten species encapsulated in the skeleton of SBA-16. A bimodal pore diameter distribution occurs from the pore diameter distributions of the samples (Figure 4); the first peak reflects the size of the mesopore entrance that interconnects the ordered mesopores, and the second peak represents the pore diameter of the ordered cage-like pores.^[48] With increased tungsten loading up to 15.51 wt%, the S_{BET}, V_{tot}, and pore diameter decrease prominently suggesting some tungsten species encapsulated in the nanocages of SBA-16. However, for the W-SBA-16(10) and W-SBA-16(5) catalysts, the pore diameters significantly increase to 6.42 and 6.52 nm, respectively; this can be assigned to massive

TABLE 1Textural properities of SBA-16 and the W-SBA-16 catalysts

Materials	Si/W ^a	W ^b (wt%)	W ^c (wt%)	S_{BET} (m ² /g)	V _{tot} ^d (cm ³ /g)	Pore diameter ^e (nm)	Total acidity (mmol NH ₃ /g)
SBA-16	∞	0	0	689	0.63	5.54	-
W-SBA-16(50)	50	9.97	9.68	672	0.61	5.42	0.33
W-SBA-16(40)	40	12.20	11.17	669	0.56	4.93	0.36
W-SBA-16(30)	30	13.04	12.99	638	0.54	4.86	0.38
W-SBA-16(20)	20	16.86	15.51	632	0.53	4.84	0.25
W-SBA-16(10)	10	28.85	21.89	500	0.44	6.42	0.21
W-SBA-16(5)	5	50.78	48.20	330	0.34	6.52	0.19

^aMole ratio of Si and W.

^bStoichiometric ratio in synthesis.

^cDerived from ICP.

^dSingle point adsorption total pore volume of pores at $P/P_0 = 0.99$.

^eBJH adsorption average pore size.



FIGURE 3 N_2 adsorption-desorption isotherms of SBA-16 and W-SBA-16 catalysts



FIGURE 4 Pore size distribution of SBA-16 and W-SBA-16 catalysts

tungsten doping because tungsten has a larger atomic radius than Si^{4+} (0.068 nm and 0.04 nm, respectively).^[49]

DR UV-Vis spectra of the W-SBA-16 catalysts are shown in Figure 5. The W-SBA-16 catalysts show two absorption bands at ~230 and ~265 nm; those two bands can be ascribed to a ligand-to-metal charge transfer in the isolated [WO₄] tetrahedral species^[50] and a charge transfer from O^{2-} to W^{6+} , which indicates the existence of a partially octahedrally coordinated tungsten oxide species in SBA-16.^[51] A band at ~380 nm for bulk WO₃ is observed in the W-SBA-16(5, 10, and 20) catalysts, and the absence of this band in the W-SBA-16(30, 40, and 50) catalysts is consistent with the results in Figure 2.

FT-IR spectra of all samples are displayed in Figure 6. Symmetric and anti-symmetric stretching bands at ~810 and ~1082 cm⁻¹ assigned to tetrahedral SiO_4^{4-} units, and



FIGURE 5 DR UV-Vis spectra of W-SBA-16 catalysts



FIGURE 6 FT-IR spectra of SBA-16 and W-SBA-16 catalysts

the Si-O-Si bending modes at ~465 cm⁻¹ are observed in all samples.^[41,52] The band at ~960 cm⁻¹ in SBA-16 is attributed to the absorption peak of the Si-OH groups.^[53,54] A typical band at ~960 cm⁻¹ is also detected in the W-SBA-16(50, 40, 30, and 20) catalysts and its intensity enhances with the increase of tungsten amount, which indicates the existence of tungsten species in the framework of SBA-16 because the band ~960 cm⁻¹ can also be attributed to the ν_{as} (Si-O-W) vibration.^[52] The decrease of the band at ~960 cm⁻¹ detected in W-SBA-16(5) and W-SBA-16(10) can be ascribed to the collapsed mesoporous framework. This destruction of the structure causes the tungsten species distributed on the surface of the matrix.^[55]

 H_2 -TPR results provide relative estimations of the reducible tungsten species in the W-SBA-16 catalysts and are displayed in Figure 7. Typical peaks of bulk WO₃ at ~650 and ~740 °C are associated with two-step

6 of 10 WILEY — Applied Organometallio Chemistry



FIGURE 7 H2-TPR profiles of W-SBA-16 catalysts

reduction $W^{6+}W^{4+} \rightarrow W^{0}$.^[56] Compared with bulk WO₃, the TP \rightarrow R patterns of the W-SBA-16 catalysts shift to higher reduction temperatures with the increase of the value of Si/W; this could be assigned to the presence of highly dispersed tungsten species that strongly interact with the silica matrix.^[44]

Temperature programmed desorption of ammonia (NH₃-TPD) was used to characterize the acidity of the W-SBA-16 catalysts. The profiles of the NH₃ desorption are presented in Figure 8 and the values of acdity are listed in Table 1. It is generally known that the distribution of acid sites is reflected by the desorption temperature of NH₃ as strong (> 400 °C), medium (250-400 °C), and weak (< 250 °C) acidic sites.^[57] As seen in Figure 8, W-SBA-16 catalysts all show a broad peak of NH₃ desorption centered at ~195-218 °C (appreciable NH₃ desorption in pure SBA-16 can not be observed.^[43]). This result suggests weak acidic sites exist in those catalysts. Moreover, the W-SBA-16 (30) catalyst exhibits two desorption peaks



FIGURE 8 NH₃-TPD profiles of W-SBA-16 catalysts

centered at ~200 and ~270 °C signifying the coexistence of weak and medium acidic sites with an acididy of 0.38 mmol/g. It can be observed that the acidity of W-SBA-16 catalysts enhances with increasing the amount of tungsten up to ~13 wt%. Further increasing the tungsten content causes the decrease of acidity. This can be ascribed to the formation of bulk WO₃.^[44,51]

3.2 | Catalytic performance of the catalysts

The catalytic activities of the immobilized W-SBA-16 catalysts, WO₃, and Na₂WO₄·2H₂O were evaluated for the oxidation of CPE with H₂O₂, and the results are provided in Table 2. Low yield (5%) of GAC is received (No. 1) when $Na_2WO_4 \cdot 2H_2O$ is used as the catalyst. SBA-16 (No. 2) shows no catalytic activity. An unexpected relatively high yield (27%) is gained (No. 3) when both Na₂WO₄·2H₂O and SBA-16 are used as the catalyst. This result can be attributed to the large mesochannels and specific surface areas of SBA-16 that can accommodate and highly disperse Na₂WO₄·2H₂O. When WO₃ acted as the catalyst (No. 4), low yield (2%) of GAC and low conversion (8.6%) of CPE are achieved. When the encapsulated W-SBA-16 catalysts are used, higher GAC vields (33-55%) are obtained. The W-SBA-16(5, 10, and 20) catalysts exhibit a lower activity than that of W-SBA-16(30, 40, and 50). The reduction in activity can be ascribed to the import of bulky WO3, which increases the resistance to the active site, and the highest yield is obtained when W-SBA-16 (30) is used as the catalyst, which can be attributed to better dispersity and greater number of active sites than for the other W-SBA-16(5, 10, 20, 40, and 50) catalysts. Na₂WO₄·2H₂O and WO₃ all exhibit poor catalytic performance, and these results indicate that the oxidation activity is mainly assigned to framework-incorporated tungsten species. According to the mechanism of the oxidation of cyclohexene^[15] and the analysis of the product distribution, CPE may be oxidized to cyclopentene oxide, and cyclopentene oxide is converted into 1, 2-cyclopentanediol. Subsequently, 1, 2cyclopentanediol is transformed into glutaraldehyde, and then glutaraldehyde is converted into GAC.

The reaction was continued for another 7 h under identical conditions, except for the absence of the catalyst, to test the heterogeneous essence of this reaction. A small increase in the conversion of CPE was observed (Table 3, No. 1, 2, and 3). This might be imputed to the existence of tungsten species in the filtrate (as confirmed using the ICP technique), corresponding to ~20, 13, and 5 wt% leaching from W-SBA-16(5, 10, and 20), respectively. However, no obvious increases in the conversion of CPE in W-SBA-16(30, 40, and 50) are observed, which clearly

TABLE 2 Oxidation of CPE to GAC catalyzed by different catalysts^a

		Conversion (%)		GAC yield	eld Selectivity (%)			
No.	Catalyst	H_2O_2	CPE	(%)	GAC	Glutaraldehyde	1,2-cyclopentanediol	Others ^b
1	Na ₂ WO ₄ ·2H ₂ O	8.3	18.8	5	27.9	20.4	12.5	39.2
2	SBA-16	-	-	-	-	-	-	-
3	Na ₂ WO ₄ ·2H ₂ O+SBA-16	35.6	47.5	27	57.7	18.7	9.6	14
4	WO ₃	4.7	8.6	2	23.2	6.1	3.3	67.4
5	W-SBA-16(5)	40.6	51.3	33	64.1	19.9	11.6	4.4
6	W-SBA-16(10)	42.7	52.4	36	68.2	18.3	8.6	4.9
7	W-SBA-16(20)	44.6	54.3	41	76.4	15.5	5.6	2.5
8	W-SBA-16(30)	56.9	69.1	55	79.5	14.4	4.4	1.7
9	W-SBA-16(40)	54.3	67.1	51	76.3	14.6	5.9	3.2
10	W-SBA-16(50)	50.4	64.9	49	75.4	15.1	6.1	3.4

 $^{a}\mathrm{H}_{2}\mathrm{O}_{2}\text{:}\mathrm{CPE}$ = 4.4:1, $\mathrm{H}_{2}\mathrm{O}_{2}$ (50 wt %, 2.99 g), catalyst amount of W = 0.065 g, 90° C, 7 h;

^bOthers, including unreacted CPE, butanedioic acid and glutaric hyaluronic acid.

TABLE 3 Heterogeneous nature of the oxidation of CPE to GAC^a

		Conversion (%)		GAC yield	Selectivity (%)			
No.	Catalyst	H_2O_2	CPE	(%)	GAC	Glutaraldehyde	1,2-cyclopentanediol	Others ^b
1	W-SBA-16(5)	48.6	61.5	43	70.7	18.2	7.3	3.8
2	W-SBA-16(10)	46.4	59.0	42	72.0	19.4	6.6	2.0
3	W-SBA-16(20)	44.1	58.9	45	76.3	16.7	4.6	2.4
4	W-SBA-16(30)	60.1	69.4	54	77.8	16.2	4.4	1.6
5	W-SBA-16(40)	56.2	67.2	52	77.5	13.6	4.0	4.9
6	W-SBA-16(50)	50.1	65.5	49	75.2	16.1	3.5	5.2

^aContinued the reaction described in Table 2 for another 7 h;

^bOthers, including unreacted CPE, butanedioic acid and glutaric hyaluronic acid.

indicate that the tungsten species in W-SBA-16(30, 40, and 50) are more stable than those in W-SBA-16(5, 10, and 20). The leaching amounts for tungsten species from the W-SBA-16(30) catalyst after recycling are shown in Figure 13.

3.2.1 | Effect of the H_2O_2 :CPE mole ratio on the oxidation of CPE

The effect of the mole ratio of H_2O_2 :CPE on the oxidation of CPE was investigated over the W-SBA-16(30) catalyst. The results are summarized in Figure 9. Lower mole ratios of H_2O_2 :CPE provide lower conversions of CPE. Increasing the H_2O_2 :CPE ratio enhances the conversion; it suggests that the high concentration of H_2O_2 is essential to support the reaction. Nevertheless, excess H_2O_2 could intensify the deep oxidation of GAC and would be costly.



FIGURE 9 Effect of H_2O_2 :CPE mole ratio on the oxidation of CPE

8 of 10 WILEY-Organometallic

Therefore, the maximum yield (55%) of GAC is obtained when the mole ratio of H_2O_2 :CPE is 4.4.

3.2.2 | Influence of the temperature on the oxidation of CPE

The influence of temperature (50-100 °C) on the oxidation of CPE with H_2O_2 was studied using the W-SBA-16(30) catalyst. Figure 10 shows that the conversion of CPE only increases by < 1% from 90 to 100 °C, which manifests that no significant benefits exist above 90°C. The selectivity of GAC decreases as the temperature increases from 90 to 100°C; the reaction system boils at the higher temperature, which may decompose GAC. Glutaric anhydride is detected by GC, which confirms this conjecture. Moreover, higher temperature (> 90°C) causes a severe decomposition of H_2O_2 . These results indicate that the optimal temperature for the oxidation of CPE is 90°C.

3.2.3 | Effect of the reaction time on the oxidation of CPE

Reaction times ranging from 3-9 h were examined for the W-SBA-16(30) catalyst, and the results are provided in Figure 11. Longer reaction times provide longer CPE conversions. The selectivity of GAC gradually decreases when the reaction time increases from 7 to 9 h. The long reaction time increases the oxidation of GAC, which can be verified by the increasing yield of butanedioic acid. To decompose as much H_2O_2 as possible, a reaction time of 7 h is optimal.

3.2.4 | Effect of the catalyst amount on the activity

The conversion of CPE increases from 31.2% to 69.1% with increasing the amount of W-SBA-16(30) from 0.1 g to 0.5 g



FIGURE 10 Influence of temperature on the oxidation of CPE





90

80

70

60

40

30

(%) ⁵⁰

FIGURE 11 Effect of reaction time on the oxidation of CPE

(Figure 12). The increased tungsten content affects the conversion of CPE and the selectivity of GAC. A maximum yield of 53% is obtained when 0.5 g of W-SBA-16(30) is used to catalyze CPE to GAC; the high catalytic performance indicates that active regions in the W-SBA-16 catalysts are easily accessible.

3.2.5 | Recycling performance of W-SBA-16 (30) catalyst for the oxidation of CPE

The W-SBA-16(30) catalyst was reused under identical circumstance to explore its stability. The leaching of tungsten, obtained by measuring the organic phase after removing the catalyst from the reaction system using the ICP technique, is shown in Figure 13. The W-SBA-16(30) catalyst can be recovered by filtration and reused three times without a significant decrease of the



FIGURE 12 Effect of catalyst amount on the activity



FIGURE 13 Reusability and regeneration of W-SBA-16 (30) catalyst

conversion of CPE or the selectivity of GAC; the catalytic activity decreases during the fourth reaction. This may be attributed to sedimentary carbonaceous species on the catalyst surface. The activity of the catalyst can be recovered by baking it under an air flow for 3 h at 550 °C; the recovered activity is comparable to that of the fresh catalyst. The leaching of tungsten is 1.01 and 0.66 wt% during the first and second uses, respectively, which rises to 0.85 wt% during the sixth use.

4 | CONCLUSIONS

We synthesized a novel heterogeneous catalyst, W-SBA-16, for oxidation of CPE to GAC. XRD and N2 adsorptiondesorption analysis show the 3D mesoporous structure of W-SBA-16. DR UV-Vis, H₂-TPR, NH₃-TPD, and ICP analysis confirm the efficient encapsulation of tungsten species on the inner pores of SBA-16, which indicates that SBA-16 can provide a suitable accommodation for tungsten species. The W-SBA-16(30, 40, and 50) catalysts are active for the oxidation of CPE with H₂O₂. Furthermore, the W-SBA-16(30) catalyst exhibits an excellent catalytic performance because the tungsten species are highly dispersed in the uniform pore channels, and more accessible active sites are exposed. Tungsten exists in isolated [WO₄] and octahedrally coordinated tungsten oxide species at all W-SBA-16 catalysts, and WO₃ crystallites exist at higher tungsten loading. The W-SBA-16(30) catalyst could be recycled using filtration or centrifugation and reused five times without considerable loss of catalytic activity, which provides the potential for industrial applications. Furthermore, when excessive tungsten is imported into SBA-16, the mesoporous structures are destroyed and the catalytic activity decreases. The optimal tungsten content is

~13 wt%. The results of this research will help to provide more valid catalysts for GAC production and to promote the oxidation of other olefins.

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10 of 10 WILEY-Organometallic Chemistry

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