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Lacunary silicotungstic heteropoly salts as high-performance catalysts in oxidation of cyclopentene

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ABSTRACT

The development of polyoxometalates for olefin oxidation is critical to achieving the green chemical process of the C5 fraction further processing. Di-lacunary silicotungstic anions were easily obtained by continuously adjusting the pH instead of the traditional step-by-step method, which exhibited excellent performance in the catalytic oxidation of cyclopentene (CPE) to aldehydes or alcohols. The 93.69% CPE conversion and 97.15% total product selectivity (41.38% for glutaraldehyde (GA) and 55.77% for 1,2-cyclopentanediol (1,2-diol) were achieved by using H_2O_2 as the oxidant and acetonitrile as the solvent. Through complementary characterization, it was found that the optimized di-lacunary silicotungstic polyoxometalate retained a complete Keggin structure, and exhibited better catalytic activity and stability than the mono-lacunary or saturated silicodecatungstate because it exposed more catalytic active centers. Furthermore, *in situ* FT-IR spectra was utilized to monitor the reaction process, revealing the formation of the active species $W(O_2)$ on the di-lacunary silicotungstic polyoxometalate and the intermediate epoxycyclopentane during the catalytic oxidation of cyclopentene.

1. Introduction

Glutaraldehyde (GA) is an essential fine chemical product and medium, widely used in disinfection chemicals, leather therapy, oilfield chemicals, and as a cross-linking agent for protein and polyhydroxy content, *etc.* [1–3]. High purity 1,2-cyclopentanediol (1,2-diol) is a high-priced specialty chemical with excellent performance [4]. The traditional technology for the industrial production of GA is the pyran method, which suffers from complicated reaction steps, limited raw material conversion, poor selectivity, and low yield, among others [5,6].

The oxidation of cyclopentene (CPE) utilizing hydrogen peroxide (H_2O_2) as an oxygen reservoir to produce GA has become the most probable technique with high value-added products from cheap and accessible raw materials [3,7,8]. In recent years, tungsten-containing immobilized catalysts such as WO_3/SiO_2 [9], WO_3/HMS [10] and W-MCM41 [2] exhibited high GA selectivity despite low CPE conversion. For the catalytic oxidation, Luo *et al.* [11] used saturated phosphotungstic acid and the phase transfer agent tetrabutylammonium bromide (TBAB). The method possessed higher conversion and selectivity, but it was difficult to recover phosphotungstic acid from water and had poor efficiency. According to previous reports [12,13], organic–inorganic polyoxometalates have been used for the oxidation of CPE to GA or 1,2-diol, and the selectivity of GA reaches 70%–80%, but the amount of these polyoxometalates used is about 1/33 (molar ratio) of CPE, which industrialization is difficult to achieve.

Polyoxotungstates have been proven to be effective in oxidizing olefins to epoxides, alcohols and aldehydes [14–17]. Among them were silicotungstic polyoxometalates, which can be applied in epoxidation reactions [18,19], particularly in olefin epoxidation reactions to produce high selectivity epoxides. Through experiments and characterization, An *et al.* [20] and Hua *et al.* [21] demonstrated that the production of active species by lacunary Keggin-type polyoxometalates with H_2O_2 was more efficient than saturated ones. The primary reasons are that lacunary Keggin-

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type polyoxometalates are easy to generate active sites and have active lattice oxygen, resulting in superior catalytic activity and stability. Simultaneously, epoxides are intermediates and essential steps in the catalytic oxidation of aldehydes or alcohols.

Based on these previous studies, the aim is to investigate the catalytic oxidation of CPE using H_2O_2 as the oxygen source to produce aldehydes and alcohols with lacunary silicodecatungstate as the catalytically active component. In the present research, the heteropolyacid quaternary ammonium salt with lacunary silicotungstate as the anion was used as the catalyst. Quaternary ammonium cation provides the phase transfer ability, improving catalytic efficiency and reducing the catalyst amount up to 1/833 (molar ratio) of CPE, simultaneously. To our knowledge, this is first report that the lacunary silicotungstic polyoxometalate is employed for the catalytic oxidation of CPE to GA. As expected, the lacunary silicotungstic polyoxometalate showed extraordinary catalytic performance in the catalytic oxidation of CPE, and it has been of great significance to improve the industrial production efficiency by reducing the catalyst amount and the reaction time in present research.

2. Experimental

2.1. Reagents

Sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, 99.5%), sodium metasilicate nonahydrate ($Na_2SiO_3{\cdot}9H_2O$, 99.5%), potassium carbonate (K_2CO_3, 99.0%), potassium chloride (KCl, 99.5%), tetrabutylammonium bromide ($C_{16}H_{36}BrN$, TBAB, 99.0%), silicotungstic acid ($H_6SiW_{12}O_{41}$, CP), cyclopentene (C_5H_8, CPE, 98.0%), acetonitrile (C_2H_3N, 99.0%) were purchased from Macklin. 1,2-Dichloroethane ($C_2H_4C_{l2}$, DCE, 99.0%), acetic acid ($C_2H_4O_2$, 99.0%), ethyl acetate ($C_4H_8O_2$, EA, 99.0%), *N,N*-dimethylformamide (C_3H_7NO, DMF, 99.0%) were purchased from Aladdin. Hydrogen peroxide (30% (mass)) was purchased from Guangzhou Chemical Reagent Factory. All chemicals are analytical purities obtained commercially and have not been further purified prior to use.

2.2. Preparation of $K_8[\gamma\text{-}SiW_{10}O_{36}]{\cdot}12H_2O$

The catalyst synthesis method was improved by continuously adjusting the pH value [22,23]. $Na_2WO_4{\cdot}2H_2O$ (18.15 g, 55 mmol) and $Na_2SiO_3{\cdot}9H_2O$ (1.42 g, 50 mmol) were dissolved in water to form solutions A and B, respectively. 16.5 ml of 4 mol·L^{-1} HCl solution was added to solution A while vigorously stirring (drip time was controlled within 0.17–0.25 h). Solution B was poured into solution A, and a small amount of 4 mol·L^{-1} HCl solution was added to adjust the pH range between 5 and 6 and maintained for 1.67 h. Afterwards, a 2 mol·L^{-1} K_2CO_3 solution was added to adjust the pH value of the system to about 9.1, and kept it for 0.27 h. A white solid precipitate was obtained by filtration, washed with 1 mol·L^{-1} KCl solution and air dried at 80 °C. Yield: 42.82%.

2.3. Preparation of $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$

The samples were weighed in accordance with the molar ratio of $K_8[\gamma\text{-}SiW_{10}O_{36}]{\cdot}12H_2O$ to TBAB of 1:11. 4 g $K_8[\gamma\text{-}SiW_{10}O_{36}]{\cdot}12H_2O$ was dissolved in 40 ml of water and adjusted to pH = 2.0 ± 0.1 with dilute HNO_3 solution to form solution C. After stirring for 0.25 h at room temperature, 1.8 g TBAB was added to solution C. A white precipitate was rapidly produced after mixing uniformly. The white precipitate was collected by filtration and washed with distilled water. The white solid $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ was obtained after purification (the white solid was dissolved in acetonitrile and precipitated with a large amount of water). IR spectrum (KBr, cm^{-1}): 3437, 2962, 2874, 1635, 1485, 1382, 1009, 967, 921, 883, 805, 754, 553. calcd for $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$: C, 22.48%; H, 4.33%; N, 1.64%; Si, 0.82%; W, 53.86%; Found: C, 21.86%; H, 4.26%; N, 1.59%; Si, 0.85%; W, 53.96%. Yield: 97.90%.

The above methods were followed to prepare mono-lacunary silicotungstic polyoxometalate ($(Bu_4N)_8[\beta_2\text{-}SiW_{11}O_{39}]$) using $K_8[\beta_2\text{-}SiW_{11}O_{39}]{\cdot}14H_2O$ as the raw material.

The procedures were followed to make saturated silicotungstic polyoxometalate ($(Bu_4N)_4SiW_{12}O_{40}$) using saturated silicotungstic acid as the raw material.

The preparation of $K_8[\beta_2\text{-}SiW_{11}O_{39}]{\cdot}14H_2O$ was shown in the Supplementary Material.

3. Results and Discussion

3.1. Catalyst characterization

As shown in Fig. 1, compared with the reference substance of saturated silicotungstic acid, the synthesized intermediates $K_8[\beta_2\text{-}SiW_{11}O_{39}]{\cdot}14H_2O$ and $K_8[\gamma\text{-}SiW_{10}O_{36}]{\cdot}12H_2O$ and the lacunary silicotungstic polyoxometalate $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ displayed the characteristic absorption peaks of typical Keggin-type polyoxometalate at 700–1100 cm^{-1}. The di-lacunary anion intermediate of $K_8[\gamma\text{-}SiW_{10}O_{36}]{\cdot}12H_2O$ divided its vibrational absorption peak at 906 cm^{-1} and 867 cm^{-1}. Essentially, the anion lose WO_4^+ to create the lacunary position, resulting in the anion structure having a worse symmetry [24]. After adding tetrabutylammonium bromide, the characteristic peak of lacunary silicotungstic polyoxometalate of $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ shifted to higher or lower wavenumbers. The major reason was that the radius of the quaternary ammonium cation was larger than that of H^+, and the volume effect of cations caused a change in the electron distribution in the molecule, modified the force constant of the chemical bond and caused the characteristic peak of the group shift [25].

Since charge transfer from the oxygen atom to the tungsten atom caused ultraviolet (UV) absorption, the heteropoly anions with the Keggin structure showed two characteristic absorption peaks at around 200 nm and 260 nm, belonging to charge transfer from $O_d \rightarrow W$ in $W{=}O_d$ bond and $O_b/O_c \rightarrow W$ [26]. The character-

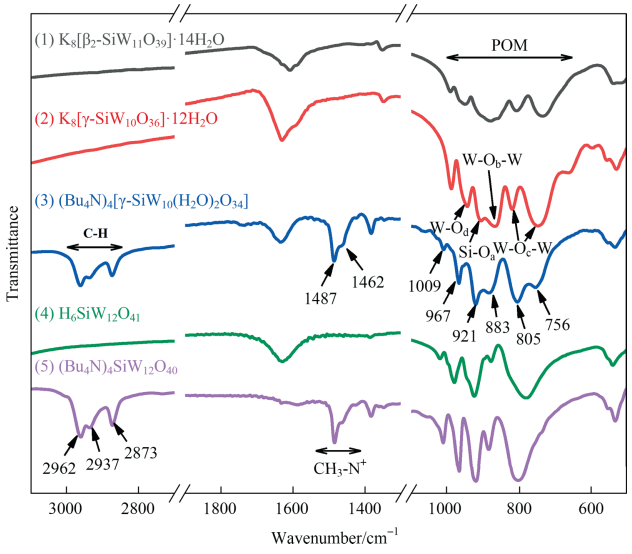

Fig. 1. FT-IR spectra of different silicotungstic heteropoly salts and their intermediates.

istic absorption peaks of saturated silicotungstic acid with Keggin structure were observed at 198 nm and 263 nm in Fig. 2. The synthesized lacunary silicotungstic polyoxometalate had absorption peaks at 196 nm and 269 nm. It can be concluded that the synthesized compound had a Keggin structure. Furthermore, two intermediates of potassium salts γ-SiW_{10} and β_2-SiW_{11} showed a charge transition of $O_d \rightarrow W$ at 198 nm. The charge transitions of $O_b/O_c \rightarrow W$ appeared at 259 nm and 255 nm, respectively. Therefore, the synthesized lacunary silicotungstic quaternary ammonium salts and their intermediates maintained the Keggin structure.

As shown in Fig. 3, under the reference of the saturated silicotungstic acid standard, the diffraction peaks of mono/di-lacunary silicotungstates were essentially coincidental, and the diffraction peaks were located at 8°–10°, 16°–23°, 25°–30° and 31°–38°, respectively, which were similar to those of the γ-SiW_{10} reported in Ref. [27], indicating that the precursor of lacunary Keggin-type silicotungstic polyoxometalate formed an effective crystal structure. The diffraction peaks of $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12H_2O$ and $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ were essentially coincidental, indicating that the cation exchange had no major effect on the crystal structure of γ-SiW_{10}. However, in Fig. 3, the diffraction peak of $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ was relatively flat, owing to the weakening effect of the quaternary ammonium cation on the diffraction peak of the anions [28].

3.2. Catalytic performance

3.2.1. Catalytic response of silicotungstate in cyclopentene oxidation

Oxidation of cyclopentene has been performed various silicotungstate catalysts including saturated, mono-lacunary and di-lacunary silicotungstates and its quaternary ammonium salts in acetonitrile at 35 °C.

The UV of the four catalysts in Fig. 4 revealed that the charge transition of $O_b/O_c \rightarrow W$ is observed at 260 nm. The transition energies of the four catalysts were listed in the following order: saturated silicotungstic acid > $(Bu_4N)_4SiW_{12}O_{40}$ > $(Bu_4N)_8[\beta_2\text{-}SiW_{11}O_{39}]$ > $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$. Since the essence of charge transfer was the redox process inside the molecule, the charge transfer band energy of the compound was intrinsically related to the redox properties of the ions constituting the molecule [25]. The lower the transition energy $O_b/O_c \rightarrow W$, the easier it was to reduce. Therefore, it can be assumed that the sequence of the oxidizing ability of various lacunary silicotungstate anions

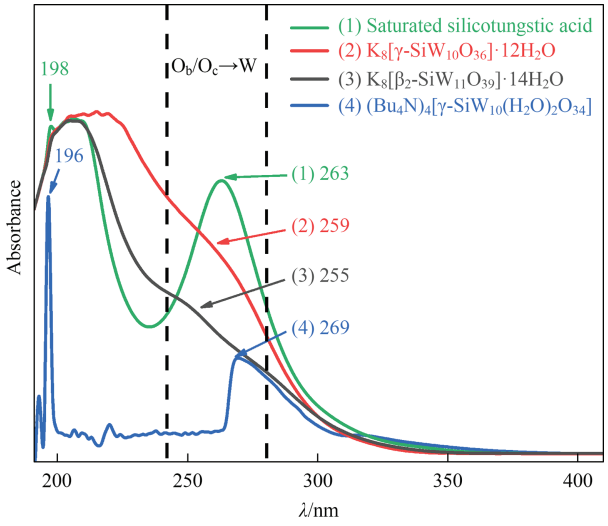

Fig. 2. UV spectra of pure silicon tungsten acid and synthetic silicotungstate.

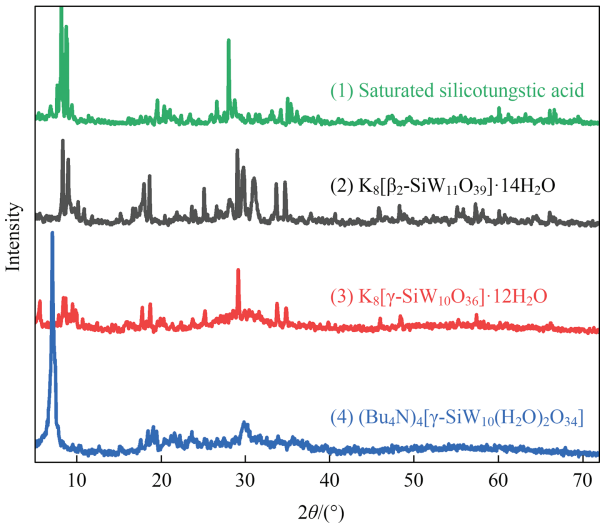

Fig. 3. XRD patterns of pure silicotungstic acid and synthetic silicotungstates.

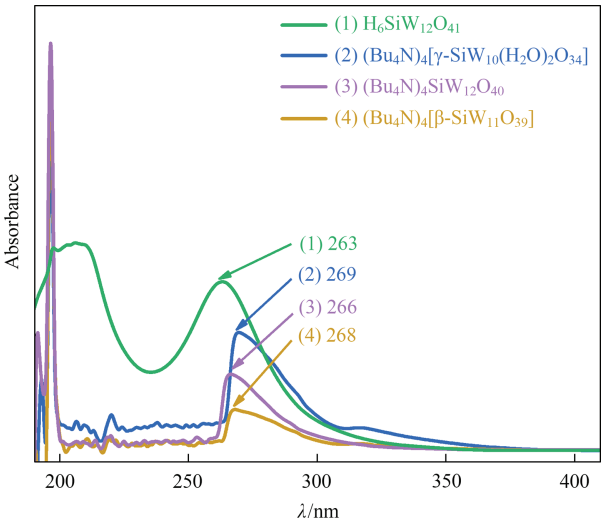

Fig. 4. UV spectra of four catalytic substances.

was $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ > $(Bu_4N)_8[\beta_2\text{-}SiW_{11}O_{39}]$ > $(Bu_4N)_4\text{-}SiW_{12}O_{40}$ > saturated silicotungstic acid.

X-ray crystallography were conducted to characterize crystal structures of two lacunary silicotungstic anions including $[SiW_{10}O_{36}]^{8-}$ and $[SiW_{12}O_{40}]^{4-}$, which were comparable to those reported in the literature [29]. As shown in Fig. 5, the ball-and-stick model exhibited the di-lacunary silicotungstic anions $[SiW_{10}O_{36}]^{8-}$ lost two WO_6 octahedra, resulting in the formation of new terminal oxygen after the oxygen originally located in the WO_6 octahedra junction were lost, and new active sites were formed.

Table 1 showed the results of a series of silicotungstic polyoxometalate catalysts and the reported catalysts for the oxidation of cyclopentene. At present, most reports on the one-step cyclopentene oxidation were performed with elemental or oxide materials containing tungsten or niobium, *tert*-butanol (TBA) or dichloroethane (DCE) as a solvent, and 30%–50% (mass) H_2O_2 solution as the oxidant. The comparison results showed that $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ had the advantages of shorter reaction time (5 h) and higher overall product selectivity (>96%) than 10%Nb-SBA-15, 35%HPWs@UiO-66, Nb_2O_5/MCM-41 (entries 1,2,5). Compared with $H_3PW_{12}O_{40}$ and $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3PW_4O_{16}$ (entries 3,4), $(Bu_4N)_4[\gamma\text{-}$

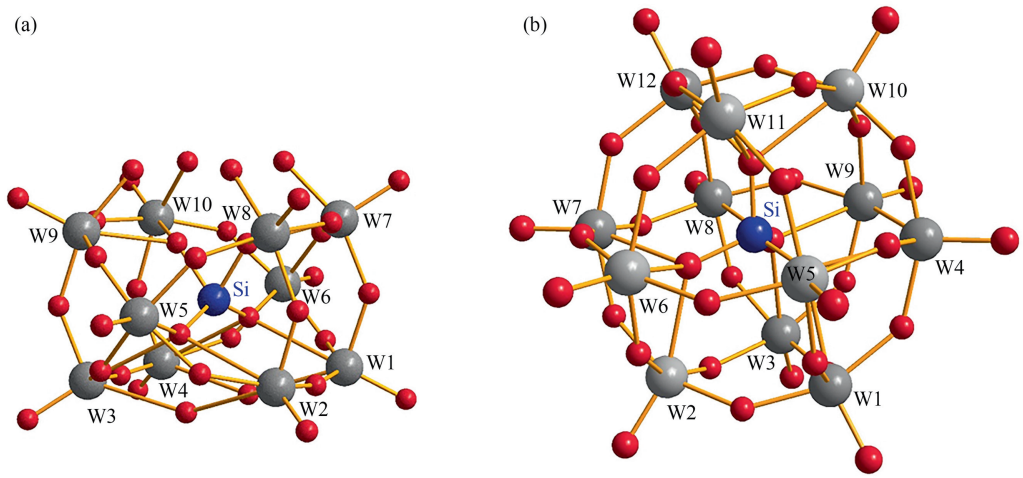

Fig. 5. Ball-and-stick structure of (a) lacunary silicotungstate and (b) saturated silicotungstate. Crystal data for lacunary silicotungstate: $C_{64}H_{144}O_{36}N_4H_2SiW_{10}$; Mr = 3412, cubic, space group, Im 3m, a = 17.7805(7) nm, b = 17.7805(7) nm, c = 17.7805(7) nm, $\alpha = \beta = \gamma = 90.00°$, V = 5621.2(4) nm^3, Z = 1, R_1 = 0.0413, wR_2 = 0.1236.

Table 1
Oxidation of cyclopentene with H_2O_2 catalyzed by various catalysts

Entry	Catalyst	Reaction conditions	Catalytic performance	Ref.
1	10%Nb-SBA-15	30% (mass) H_2O_2, TBA, 35 ℃, 24 h	C_{CPE} = 87.00%, S_{GA} = 62.00%	[3]
2	35%HPWs@UiO-66	30% (mass) H_2O_2, TBA, 35 ℃, 24 h	C_{CPE} = 94.80%, S_{GA} = 82.60%, $S_{1,2\text{-diol}}$ = 3.1%	[8]
3	$H_3PW_{12}O_{40}$ + TBAB	30% (mass) H_2O_2, DCE, 35 ℃, 4 h	C_{CPE} = 59.80%, S_{GA} = 38.00%, $S_{1,2\text{-diol}}$ = 55.60%	[11]
4	$[\pi\text{-}C_5H_5NC_{16}H_{33}]_3PW_4O_{16}$	30% (mass) H_2O_2, DCE, 35 ℃, 8 h	C_{CPE} = 100%, S_{GA} = 78.00%	[13]
5	Nb_2O_3/MCM-41	50% (mass) H_2O_2, ethanol, 35 ℃, 24 h	C_{CPE} = 100.00%, S_{GA} = 50.00%	[30]
6	$(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{36}(H_2O)_2]$①	30% (mass) H_2O_2, acetonitrile, 35 ℃, 5 h	C_{CPE} = 93.69%, S_{GA} = 41.38%, $S_{1,2\text{-diol}}$ = 55.77%	This work
7	$(Bu_4N)_8[\beta_2\text{-}SiW_{11}O_{39}]$①	30% (mass) H_2O_2, acetonitrile, 35 ℃, 6 h	C_{CPE} = 91.43%, S_{GA} = 20.33%, $S_{1,2\text{-diol}}$ = 55.94%	This work
8	$(Bu_4N)_4SiW_{12}O_{40}$①	30% (mass) H_2O_2, acetonitrile, 35 ℃, 6 h	C_{CPE} = 85.98%, S_{GA} = 0.00%, $S_{1,2\text{-diol}}$ = 0.00%	This work
9	$H_6SiW_{12}O_{41}$①	30% (mass) H_2O_2, acetonitrile, 35 ℃, 6 h	C_{CPE} = 91.21%, S_{GA} = 10.00%, $S_{1,2\text{-diol}}$ = 6.17%	This work

① Reaction conditions: catalyst 0.03 mmol, acetonitrile 4 ml, cyclopentene 25 mmol, H_2O_2 (30% (mass)) 30 mmol; stirring speed: 500 r·min^{-1}.

$SiW_{10}(H_2O)_2O_{34}$] was an efficient catalyst for the cyclopentene oxidation, which can effectively improve the CPE conversion (>90%). Saturated silicotungstic acid and its quaternary ammonium salt (entries 8,9) had minimal reactivity to produce aldehydes or alcohols. Because the catalytic oxidation of CPE to GA was a multi-step reaction. Under the action of the peroxide W(O_2), CPE was epoxidized to produce epoxycyclopentane, and then, further oxidized to aldehydes and alcohols under the action of the nucleophilic reagents H_2O_2 or H_2O [9,11]. Saturated silicotungstic acid and its quaternary ammonium salt have been reported to show little activity in the key step of olefins epoxidation [29]. The CPE conversion and total products selectivity of the lacunary quaternary ammonium salt catalysts (entries 6,7) were increased to 90%–99% and 75%–95%, respectively, at reaction times of 5–6 h, demonstrating the superior ability of cyclopentene oxidation to aldehydes or alcohols. In a conclusion, the lacunary polyoxometalate anions of $[SiW_{10}O_{36}]^{8-}$ with more oxygen vacancies exposing more active sites facilitate the enhancement of cyclopentene conversion, and more target products would be produced consequently [20,21].

3.2.2. Solvent effect on cyclopentene oxidation

The effect of various solvents in the oxidation of cyclopentene was evaluated under the same reaction conditions of molar ratio of reagents, temperature, and time in Table 2. Farnetti and DiMonte proposed that the catalysts are more active and selective in a homogeneous system than in heterogeneous systems [31]. CPE is a slightly polar molecule (μ = 0.9D) [32]. DMF is a potentially basic medium with nonhydrogen bonded and highly polar [33]. The homogeneity of the reaction system in DMF improved the conversion of CPE and the selectivity of epoxycyclopentane. However, its weak basicity could not conducive to the continuous oxidation to aldehyde or alcohol. The polar protic solvent acetic acid and hydrogen peroxide can easily formed peracetic acid, which improved the oxygen transport capacity and achieved a CPE conversion of 99.62%. However, the overall range of the product was poor, possibly due to over-oxidation of aldehydes or alcohols to acids. Two phase were observed in the low polar solvents 1,2-dichloroethane and ethyl acetate. The low solubility of hydrogen peroxide in the aqueous layer in the above two solvents made the reaction slower and the conversion lower. When acetonitrile capable of dissolving $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$, was used as a solvent, the catalytic oxidation reaction exhibited the best conversion of CPE (98.2%), selectivity of GA (29.64%) and selectivity of 1,2-diol (61.18%). Acetonitrile is a strong polar aprotic solvent that makes it a suitable solvent for this homogeneous system containing a slightly polar substrate (CPE) and aqueous oxidant (H_2O_2). The ability of hydrogen peroxide to transfer oxygen atoms to CPE was enhanced by promoting the conversion of metal peroxy intermediates into reactive oxygen species [34]. The effect of molar ratio of catalyst and H_2O_2 to CPE on oxidation of CPE when acetonitrile was used as the solvent will be presented later.

3.2.3. The stability of catalyst

As the water content of the reaction system increased, the solid catalyst was separated from the solvent, and it can be easily removed by rotary vacuum evaporation, centrifuged and recycled for reaction. New catalysts were added and consistent experimental conditions were maintained throughout the experiment. Fig. 6 (a) showed the catalytic oxidation experiment of CPE. After six rounds, the conversion of CPE remained around 90%, the selectivity

Table 2
Oxidation of cyclopentene catalyzed by γ-SiW_{10} catalyst under various solvents

Entry	Solvent	Conversion of CPE/%	Selectivity/%	
			GA	1,2-diol
1	*N*,*N*-dimethylformamide	87.56	0.00	0.00
2	Acetonitrile	98.20	29.64	61.18
3	Acetic acid	99.62	17.65	46.02
4	Ethyl acetate	63.08	10.46	40.98
5	Dichloroethane	76.32	21.85	57.55
6	No solvent	90.98	20.21	62.21

Reaction conditions: catalyst $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ 0.03 mmol, acetonitrile 4.00 ml, cyclopentene 25 mmol, H_2O_2 (30% (mass)) 37.50 mmol, temperature 35 °C, reaction time 5 h, stirring speed 500 r·min^{-1}.

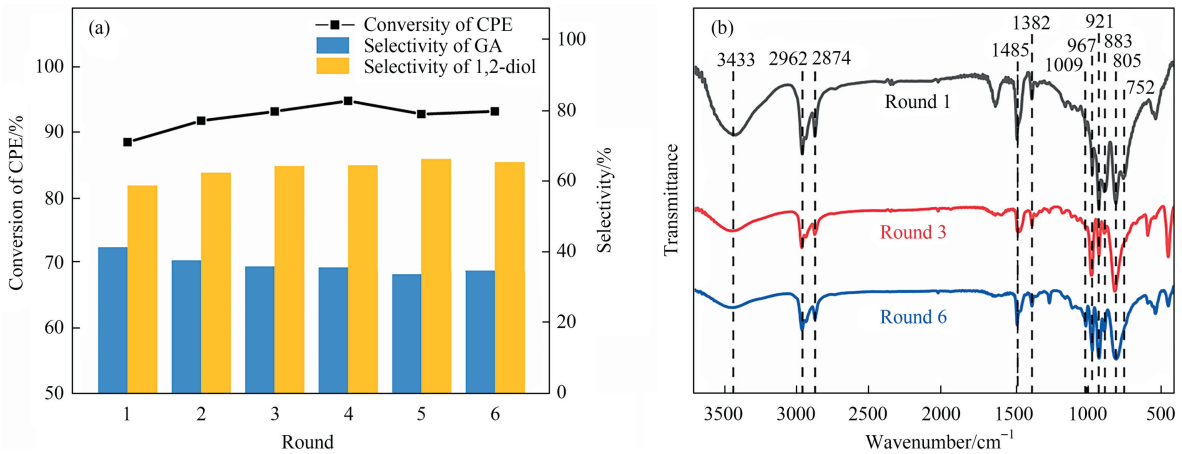

Fig. 6. (a) Recirculating catalyst activity test; (b) IR spectra of recirculating catalyst after three cycles. Reaction conditions: catalyst $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ 0.03 mmol, acetonitrile 4.00 ml, cyclopentene 25 mmol, H_2O_2 (30% (mass)) 30 mmol; temperature 35 °C, reaction time 5 h, stirring speed 500 r·min^{-1}. Catalysts are added only the first time.

of GA was around 30% and the selectivity of 1,2-diol was around 60%. Fig. 6(b) showed the IR of the recovered catalyst after the first, third and sixth cycle experiments. The symmetric and asymmetric stretching vibration peaks of CH_3—N^+ were maintained at 1485 cm^{-1} and 1387 cm^{-1}, and the stretching vibrations of —CH_2 group of tetrabutylammonium were maintained at 2962 $cm^{-1}$and 2874 cm^{-1}. The stretching vibration peaks of W=O_d were kept at 1009 cm^{-1} and 967 cm^{-1}, and $\bar{\nu}$(Si—O_a) = 921 cm^{-1}, $\bar{\nu}$(W—O_b—W) = 883 cm^{-1} and $\bar{\nu}$(W—O_c—W) = 805 cm^{-1} were retained, indicating that the catalyst structure was complete. The above results proved that the resultant catalyst was stable enough for the oxidation of CPE to alcohol or aldehyde.

3.3. In situ FT-IR spectroscopy for catalytic oxidation of CPE

3.3.1. Effect of molar ratio of catalyst to CPE

To further reveal the conversion pathways of the catalytic oxidation of CPE, *in situ* FT-IR was used to dynamically monitor the reaction process. The effect of the amount of catalyst on catalytic oxidation was shown in Fig. 7. The O—O stretching vibration peak (842 cm^{-1}) of W(O_2) structure and the stretching vibration peak (967 cm^{-1}) of terminal oxygen W=O_d in heteropoly anions were associated with the generation and consumption of active species. As shown in Fig. 7(a), the intensity of the peak at 842 cm^{-1} was the strongest at *n*(Cat.): *n*(CPE) = 0.0006:1 after 2 h and the intensity of the peak recovered at 967 cm^{-1} was the strongest at *n*(Cat.): *n*(CPE) = 0.0014:1 when the reaction end time was 5 h. It indicated that the terminal oxygen W=O_d in $[\gamma\text{-}SiW_{10}O_{36}(H_2O)_2]^{8-}$ anions reacted with H_2O_2 to form a peroxide complex W(O_2) with oxidation activity. Other types of tungsten-containing heteropoly acids have been reported [11,35]. The organic quaternary ammonium cation (tetrabutyl ammonium cation) not only served as supports for heteropoly acid compounds to optimize their solubility and stability in the solvent, but also provided a suitable hydrophobic-hydrophilic equilibrium surface microenvironment in the catalytic interface, that was, to enhance the contact between the hydrophobic cyclopentene in the oil phase and the hydrophilic H_2O_2 molecules in the water phase, thereby promoting the epoxidation of olefins catalyzed by the active species W(O_2) to form the intermediate epoxycyclopentane. The C—O—C stretching vibration peak of epoxides was around 1125 cm^{-1} [4], and it had three characteristic absorption peaks, namely 8μ peak, 11μ peak, 12μ peak, respectively in 1253 cm^{-1}, 948 cm^{-1}, 802 cm^{-1}. With time increased, it reached the maximum points in 0–2 h and then gradually disappeared, indicating the formation and consumption of epoxycyclopentane. Fig. 7(b) showed the peak shape changes of cyclopentene ($\bar{\nu}$(C=C) = 1614 cm^{-1}, $\bar{\nu}$(—CH_2) = 2946 cm^{-1}, 2847 cm^{-1}, $\bar{\nu}$(=CH) = 3054 cm^{-1}), glutaraldehyde ($\bar{\nu}$(—CH_2 connected to —CO—) = 1614 cm^{-1}) and 1,2-cyclopentadiol ($\bar{\nu}$(C—O) = 1086 cm^{-1}). When the catalyst dosage was increased up to *n*(Cat.):*n*(CPE) = 0.0012:1, the conversion of CPE reached 93.69%, and the selectivity of GA and 1,2-diol increased to 41.38% and 55.77%, respectively. As the amount of catalyst increased, the conversion of CPE tended to balance out and the selectivity decreased. One possible explanation for this was that as the amount of catalyst was increased, the water in the system (water in H_2O_2/generated water) precipitated and agglomerated excess catalysts, which was not conducive to diffusion [11,36].

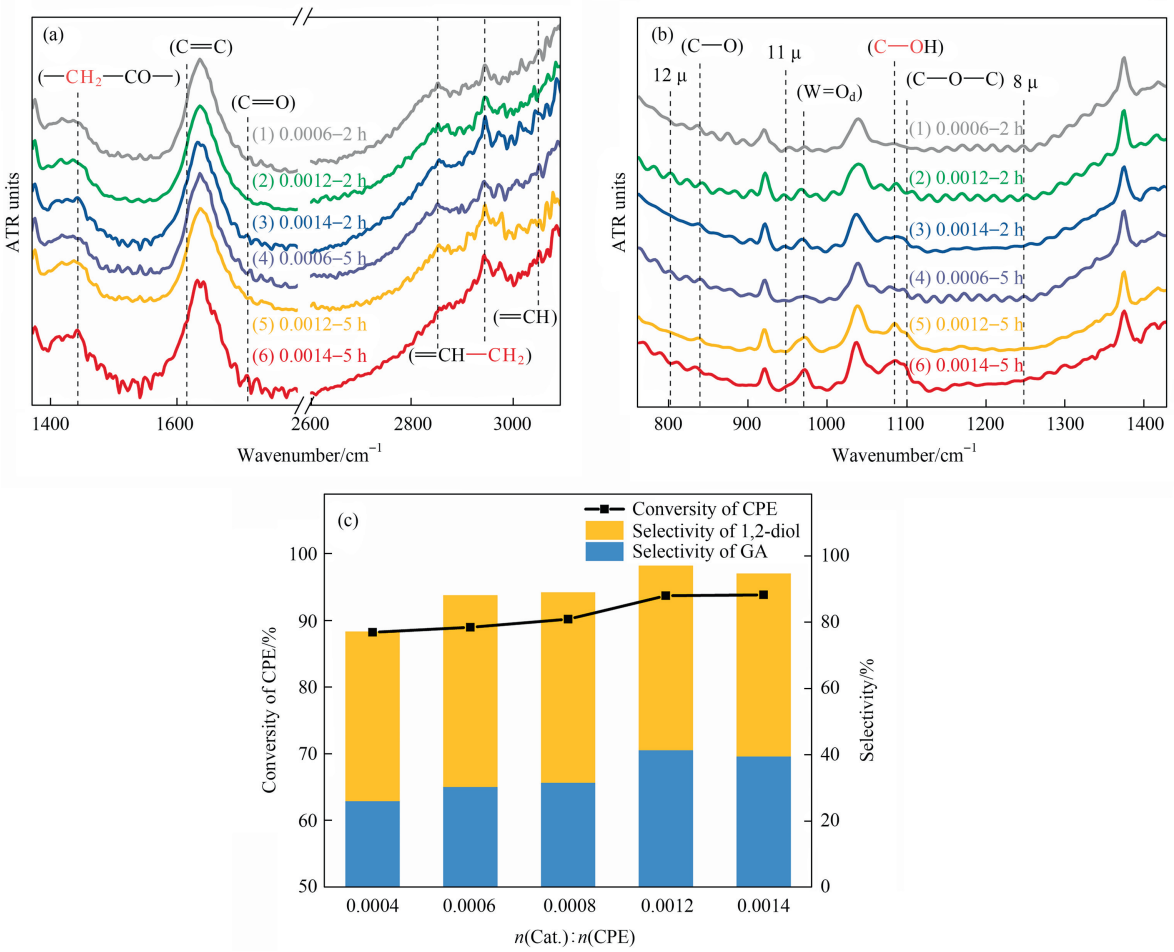

Fig. 7. (a) *In situ* FT-IR taken during catalytic oxidation of CPE in acetonitrile in different catalyst proportions in the 800–1400 cm^{-1} region; (b) *In situ* FT-IR taken during catalytic oxidation of CPE in different catalyst proportions in the 1400–3100 cm^{-1} region; (c) Influence of the catalyst ratio on the distribution of CPE and products. Reaction conditions: catalyst $(Bu_4N)_4$ [γ-$SiW_{10}(H_2O)_2O_{34}$], acetonitrile 5.00 ml, cyclopentene 31.25 mmol, H_2O_2 (30% (mass)) 31.25 mmol, temperature 35 °C, reaction time 5 h, stirring speed 500 r·min^{-1}.

3.3.2. Effect of molar ratio of H_2O_2 to CPE

The first function of H_2O_2 was to stimulate the catalytic active center W═O to produce peroxide species for the epoxidation of CPE to form epoxycyclopentane, and the second function was to effect peroxide hydrolysis of intermediate epoxides after epoxidation of CPE to obtain aldehydes or alcohols [5]. Fig. 8 depicted the effect of H_2O_2 amount on catalytic oxidation. The peak intensity of the original $W(O_2)$ structure and the recovered terminal oxygen structure $W{=}O_d$ were the strongest with $n(H_2O_2)$:n(CPE) = 1.0:1, and the conversion of H_2O_2 reached 93.35%, as shown in Fig. 8 (a). When the amount of H_2O_2 was low, the formation of $W(O_2)$ and epoxides was reduced, and cyclopentene was only partially oxidized, resulting in a low conversion (less than 80%). It was worth noting that epoxides have high reactivity owing to cyclic tension and were also sensitive to nucleophilic reagents. The water in the system (or water from H_2O_2) was used as a nucleophilic reagent to oxidize epoxycyclopentane to 1,2-diol. The C—O stretching vibration of 1,2-diol (1086 cm^{-1}) increased with time, indicating that the intermediate was converted alcohol. As displayed in Fig. 8(c), with the amount of H_2O_2 increased ($n(H_2O_2)$: n (CPE) > 1.0:1), the conversion of CPE was gradually balanced and reached more than 90%, while the selectivity of GA decreased significantly (by 10%). It indicated that too much H_2O_2 caused the deep oxidation of the target product to the by-products glutaric acid and γ-aluronic acid, and that the higher water content and more epoxycyclopentane made it easier for the epoxides to react with water to from 1,2-diol [11,37].

3.4. Discussion on possible reaction mechanism

On the basis of all the results, we proposed a possible reaction mechanism for the selective partial oxidation of CPE with hydrogen peroxide by $(Bu_4N)_4$[γ-$SiW_{10}(H_2O)_2O_{34}$] in acetonitrile. As illustrated in Fig. 9, [γ-$SiW_{10}(H_2O)_2O_{34}]^{4-}$ reacted with hydrogen peroxide to from the diperoxo species [γ-$SiW_{10}O_{32}(O_2)_2]^{4-}$. The isolated compound [γ-$SiW_{10}O_{32}(O_2)_2]^{4-}$ was inactive for epoxidation of C═C bond of the cyclopentene and needed to react further with hydrogen peroxide to from the active oxygen species $W(O_2)$ that served as active components in this process [11,38]. The phase-transfer agent $(Bu_4N)^{4+}$ served as an intermediator that bring the "active oxygen" from the aqueous phase to organic phase. The oxygen atom of $W(O_2)$ transferred to the C═C double bond, giving the corresponding epoxide to from the intermediate epoxycyclopentane and further to from GA. Finally, the active oxygen species was disappeared and regenerated by reaction with hydrogen peroxide. However, the intermediate epoxycyclopentane was oxidized into another product 1,2-diol When water was used as nucleophilic reagent [13].

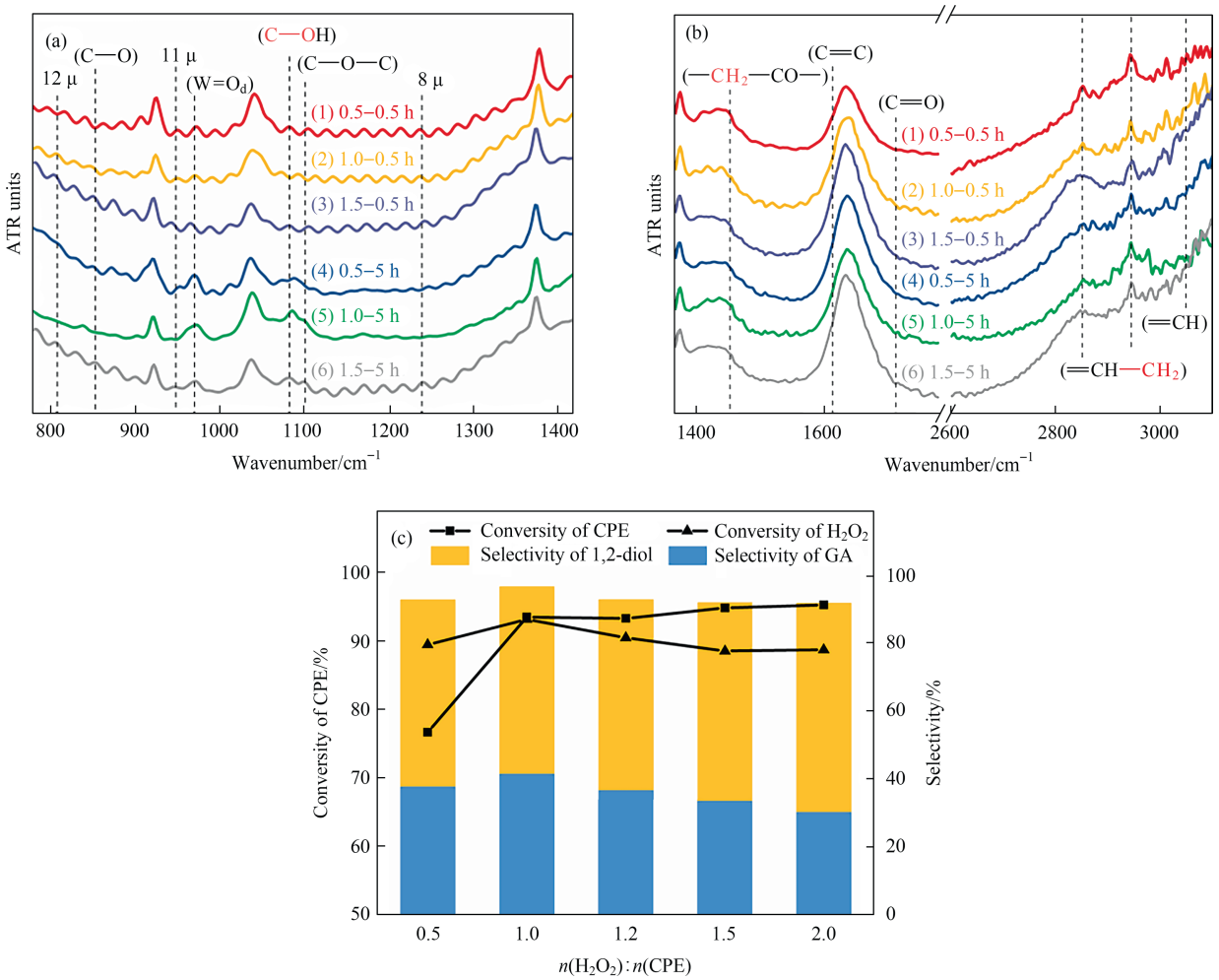

Fig. 8. (a) *In situ* FT-IR taken during catalytic oxidation of CPE in acetonitrile in different ratios of H_2O_2 in the 800–1400 cm^{-1} region; (b) *In situ* FT-IR taken during catalytic oxidation of CPE in different ratios of H_2O_2 in the 1400–3100 cm^{-1} region; (c) Influence of the H_2O_2 ratio on the distribution of CPE and products. Reaction conditions: catalyst $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ 0.038 mmol, acetonitrile 5.00 ml, cyclopentene 31.25 mmol, temperature 35 °C, reaction time 5 h, stirring speed 500 r·min^{-1}.

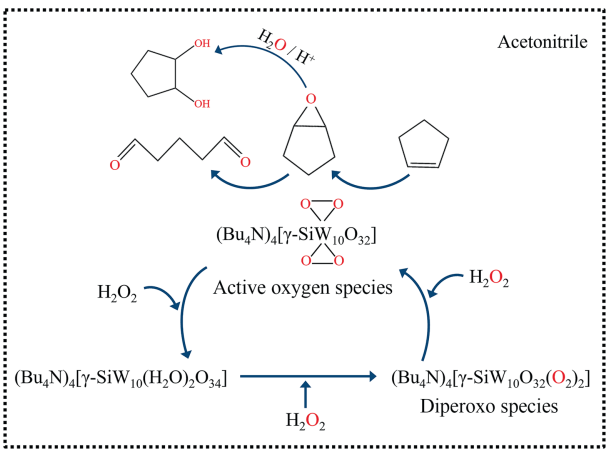

Fig. 9. Possible mechanism for the oxidation of CPE with H_2O_2 by $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ in acetonitrile.

4. Conclusions

In summary, the present research fabricated a novel di-lacunary silicotungstic quaternary ammonium salt, which was a highly effective catalyst for the catalytic oxidation of CPE to aldehydes or alcohols. *In situ* FT-IR spectra revealed the formation of active species $W(O_2)$ on the di-lacunary silicotungstic polyoxometalate and the intermediate epoxycyclopentane during the catalytic oxidation of CPE to GA. Furthermore, it was discovered that the total product selectivity was significantly improved with the increase of the active species formed in the catalyst. The addition of H_2O_2 was beneficial for the reaction between water as a nucleophilic reagent and epoxycyclopentane to produce 1,2-cyclopentadiol. Under the conditions of $n(H_2O_2)$: n(CPE) = 1:1, n(Cat.):n(CPE) = 0.0012:1, reaction temperature of 35 °C for 5 h in acetonitrile, the conversion of CPE reached 93.69%, the selectivity of GA and 1,2-diol reached 41.38% and 55.77%, respectively. The resultant catalyst $(Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$ exhibited robust stability in recycling experiments, which is crucial in practical applications for the catalytic oxidation of CPE.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary material to this article can be found online at https://doi.org/10.1016/j.cjche.2022.07.004.

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