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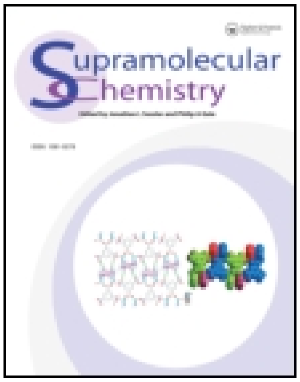

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Enhanced catalytic activity and recyclability for oxidation of cinnamaldehyde catalysed by β-cyclodextrin cross-linked with chitosan

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Enhanced catalytic activity and recyclability for oxidation of cinnamaldehyde catalysed by β-cyclodextrin cross-linked with chitosan

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Selective oxidation of cinnamaldehyde to benzaldehyde under mild conditions has been carried out for the first time in aqueous phase with β-cyclodextrin–chitosan polymer (β-CD–CTS) as a heterogeneous catalyst. Compared with β-cyclodextrin polymer (β-CDP) catalyst, β-CD–CTS showed significant promotion for the oxidation of cinnamaldehyde to benzaldehyde, in which 78% yield of benzaldehyde could be obtained. In addition, the mechanism of the oxidation was proposed according to the experimental results and theoretical calculation. The results indicated that chitosan had played a key role, and the significant promotion of conversion and selectivity for the oxidation could be attributed to inclusion complex formed via intermolecular weak interactions, e.g. hydrogen bonding between cinnamaldehyde and β-CD–CTS. The heterogeneous catalyst could be reused, and its catalytic efficiency remained unchanged, which suggests that the catalyst is efficient for the oxidation of cinnamaldehyde. The results reported herein may be a promising method for the production of benzaldehyde from natural cinnamaldehyde.

Keywords: selective oxidation; β-cyclodextrin–chitosan polymer; benzaldehyde; mechanism; kinetics

1. Introduction

In recent years, the use of efficient catalysts for the manufacture of fine chemicals has attracted much attention due to environmental safety. The heterogenisation of catalytic systems has been a major area of research for many years due to easy separation of catalysts from products and substrates in industrial processes (*1–4*). Cyclodextrins (CDs) are a torus-shaped cyclic oligosaccharide composed of 6–8 glucopyranose units linked by glycosidic bonds (named α, β and γ-CD, respectively). It is known that CDs can form inclusion complexes with different guest molecules in aqueous solution or in the solid state through host–guest interactions (*5*, *6*). β-CD is the most abundant and most widely used among them, and has been widely used as homogeneous catalysts in various organic reactions, e.g. oxidation, reduction, ring opening and hydrolysis in aqueous solution (*7–11*).

Benzaldehyde is the second most important perfume (after vanillin), and has been widely used in cosmetics, perfumery, food and pharmaceutical industries (*12*). With increasing concern on food quality, the demand for natural benzaldehyde is growing quickly (*13*). Because of its limited supply and high price, synthesis of benzaldehyde from natural cinnamon oil, which contains more than 80% of cinnamaldehyde, has been used as a substitute of natural benzaldehyde (*14*). Recently, β-CD has been used as a homogeneous catalyst to improve the reaction selectivity for the oxidation of cinnamaldehyde to benzaldehyde (*15*). However, a large amount of solvent was required for recycling β-CD, making this process less economic for industrial application. β-CD polymer (β-CDP)-catalysed oxidation of cinnamaldehyde has been tried owing to its easy recyclability from the reaction mixture (*16*, *17*). Unfortunately, the decrease in catalytic selectivity was observed for the immobilised β-CD.

In order to overcome the problem, our newly developed immobilised β-CD, a β-cyclodextrin–chitosan polymer (β-CD–CTS, as shown in Figure 1) as a recyclable heterogeneous catalyst, exhibits much higher catalytic selectivity and stability for the oxidation of cinnamaldehyde to benzaldehyde compared with β-CDP. The improvement mechanism for the reaction selectivity was well explained. It should be mentioned that its catalytic mechanism proceeded in different ways. In addition, the process can be run in a recirculating batch reactor under mild conditions (Scheme 1). The work should be significant for the production of natural benzaldehyde.

2. Results and discussion

2.1 Structure determination

2.1.1 FT-IR characterisation

The Fourier-transform infrared spectroscopy (FT-IR) spectra of chitosan, β-CD, activated chitosan resins and β-CD–CTS are shown in Figure 2. The spectrum of

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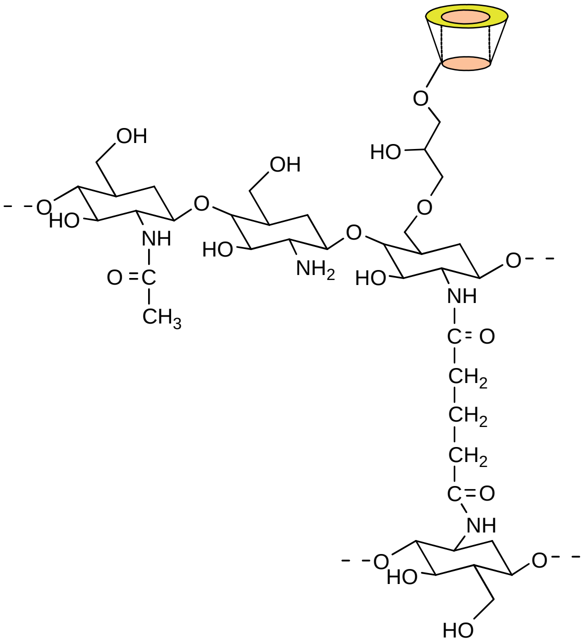
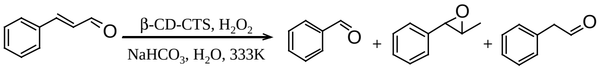


Figure 1. Structural representation of β-CD–CTS.

β-CD–CTS shows peaks ascribable to both β-CD (O—H, 3400 cm^{-1}; C—O—C, 1030 cm^{-1}) and the chitosan skeleton (N—H, 3100–3400 cm^{-1}; C═O, 1650 cm^{-1} and N—H, 1564 cm^{-1}), which is in agreement with the previously reported data (*18*).

When chitosan is cross-linked by glutaraldehyde, it can be seen that the two peaks of activated chitosan beads at 2938 and 2869 cm^{-1} are stronger than those of chitosan, indicating that a number of methyl groups are substituted into chitosan. The peak observed at 1599 cm^{-1} decreased greatly, and a sharp peak observed at 1650 cm^{-1} is attributed to the C═N vibrations of Schiff base imines. When β-CD is immobilised on activated chitosan beads using epichlorohydrin as a cross-linker, the peak at 2938 cm^{-1} is much stronger, which shows that more methyl groups are formed within the beads. The peak at 1030 cm^{-1} for β-CD–CTS is assigned to the C—O—C stretching. The increase in the band intensity at around 1030 cm^{-1} can be attributed to β-CD. In addition, the peak at 890 cm^{-1} is the characteristic bands of α-(1,4) glucopyranose in β-CD, which provides further evidence that β-CD was immobilised on chitosan beads through cross-linking with epichlorohydrin (*19*).



Scheme 1. Oxidation of cinnamaldehyde to benzaldehyde catalysed by β-CD–CTS.

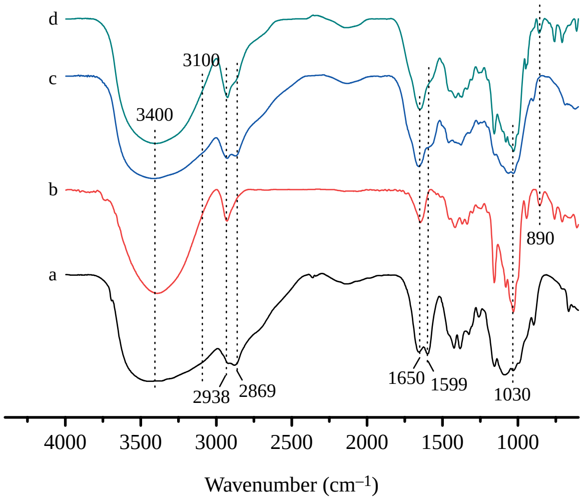


Figure 2. FT-IR spectra of chitosan (a), β-CD (b), activated chitosan resin (c) and β-CD–CTS (d).

2.1.2 *X-ray powder diffraction (XRD) results*

The XRD patterns of chitosan and β-CD–CTS are shown in Figure 3. Characteristic intense peaks at $2\theta = 10°$ and 20° were observed for chitosan due to its crystalline nature (*20*). The peaks at $2\theta = 10°$ disappeared, and the peak at $2\theta = 20°$ decreased greatly for β-CD–CTS. The results demonstrated that chemical modification of chitosan and grafting with β-CD destroyed its original crystallinity to some extent.

2.1.3 *TG results*

Thermogravimetry (TG) curves of chitosan, activated chitosan beads and β-CD–CTS are shown in Figure 4. It can be seen that chitosan exhibits three mass loss steps. The mass loss of 2% at 80°C is caused by dehydration. The second stage starts at about 260°C with mass loss of 65% due to heat decomposition of chitosan. The third stage is

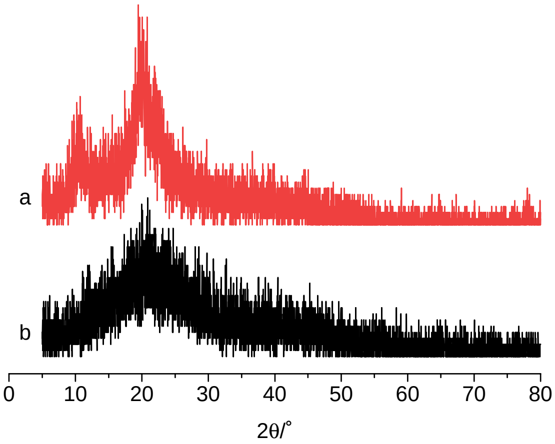


Figure 3. XRD of chitosan (a) and β-CD–CTS (b).

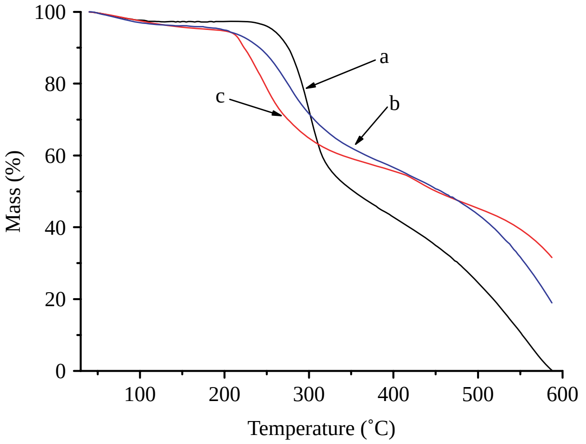


Figure 4. TGA curves of chitosan (a), activated chitosan resins (b) and β-CD–CTS (c).

the carbonisation process above 460°C with weight loss of 31%. Activated chitosan beads and β-CD–CTS show two degradation stages. The first mass loss step, from about 50 to 120°C, concerns mainly the loss of water. Thermal decompositions of activated chitosan beads and β-CD–CTS were observed in 230–580°C and 250–580°C, respectively. The second degradation stage of chitosan exhibits higher temperature (260°C) than that of activated chitosan beads (230°C) and β-CD–CTS (250°C). The result indicates that the modified chitosan is thermally less stable than chitosan due to the weak cross-linkage.

2.1.4 ^{13}C NMR results

Solid-state ^{13}C NMR spectroscopy has been considered as the most useful tool for the structural analysis of insoluble polymers (*21*).

The ^{13}C NMR spectrum of β-CD (a), chitosan (b) and β-CD–CTS (c) is shown in Figure 5, respectively. Figure 5(a) shows four ^{13}C signals between 50 and 110 ppm due to spectral overlap of some of the six carbon resonance lines from the seven α-D-glucose units. As shown in Figure 5(b), ^{13}C signals appear at δ 105.5 (C1), 79.6 (C4), 77.5 (C5), 73.0 (C3), 62.9 (C6), 59.2 (C2), 174 (C=O) and 23 ppm (CH_3). β-CD–CTS is observed to be quite similar to β-CD and chitosan in the solid state, indicating that the structure characteristics of β-CD and chitosan were well maintained in β-CD–CTS (Figure 5(c)). However, only three broad signals in the β-CD–CTS, assigned to an overlap between 50 and 110 ppm, cause a decrease in overall structural and packing order. As previously reported (*22*), the signals of epichlorohydrin cross-linked with chitosan are completely hidden by C-2,3,4 and 5 β-CD peaks. By comparing with ^{13}C NMR spectrum of chitosan and β-CD–CTS, an additional peak in the range of 135–150 ppm was observed, indicating that cross-linking reaction with glutaraldehyde occurred (*23*).

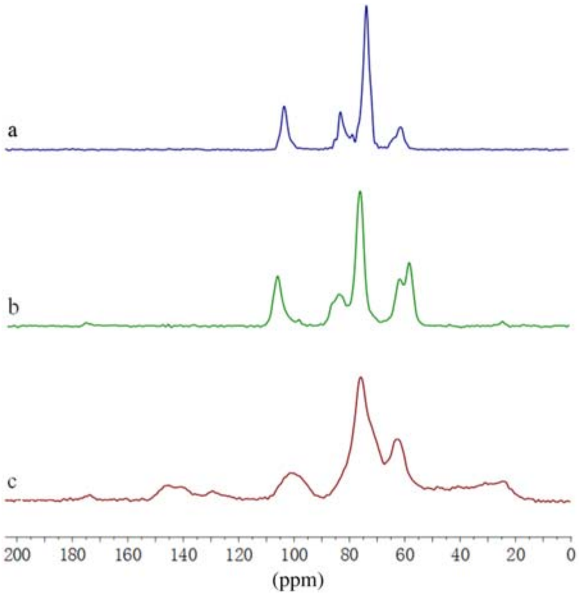


Figure 5. Solid-state NMR CP/MAS of β-CD (a), chitosan (b) and β-CD–CTS (c).

However, weak resonances at δ 174 and 24 ppm are also observable in β-CD–CTS, respectively. It is clear that the acetylated units are not involved in the cross-links.

2.2 *Reaction studies*

2.2.1 *Catalytic activities of β-CD–CTS*

As shown in Scheme 1, the oxidation of cinnamaldehyde was carried out at 60°C under 1 atm. From Figure 6, β-CD–CTS showed a significant high activity Turnover

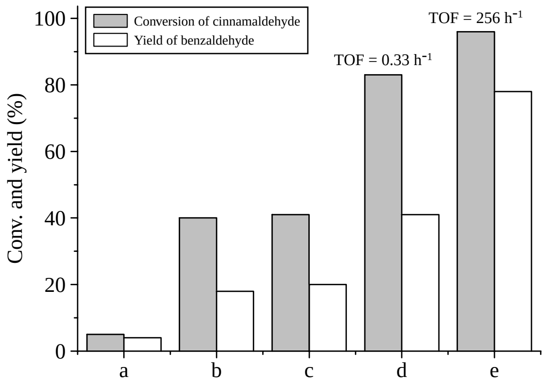


Figure 6. Catalytic activity of various catalysts: 1 mmol cinnamaldehyde, 25 ml H_2O, 60°C, 2.5 h, (a) 4 ml 30% H_2O_2 (w/w); (b) 4 ml 30% H_2O_2 (w/w), 2.5 mmol $NaHCO_3$; (c) 4 ml 30% H_2O_2 (w/w), 2.5 mmol $NaHCO_3$, 2 g chitosan; (d) 4 ml 30% H_2O_2 (w/w), 2.5 mmol $NaHCO_3$, 1 mmol β-CD; (e) 4 ml 30% H_2O_2 (w/w), 2.5 mmol $NaHCO_3$, 0.1 g β-CD–CTS (0.0015 mmol β-CD). TOF: mmol oxidised cinnamaldehyde/(mmol β-CD in the catalyst × time). Selectivity: mmol produced benzaldehyde/ mmol oxidised cinnamaldehyde.

Table 1. Effect of the different amounts of β-CD–CTS on the oxidation of cinnamaldehyde.[a]

Entry	β-CD–CTS (g)	Conversion of cinnamaldehyde (%)	Yield of benzaldehyde (%)	Yield of epoxide (%)	Yield of phenylacetaldehyde (%)
1	0	35	18	11	3
2	0.05	78	62	8	4
3	0.075	87	69	5	5
4	0.10	96	78	2	6
5	0.20	99	71	2	5

[a] Reaction conditions: 1 mmol cinnamaldehyde, 4 ml 30% H_2O_2 (w/w), 2.5 mmol $NaHCO_3$, 25 ml H_2O, 60°C, 2.5 h.

Frequency (TOF) of 256 h^{-1}) than that of β-CD (TOF of 0.33 h^{-1}) for the reaction, and 96% conversion of cinnamaldehyde and 78% yield of benzaldehyde were obtained in the presence of H_2O_2, $NaHCO_3$ and β-CD–CTS. The catalytic performance was greatly influenced by the deficiency of the above components. Only 4% cinnamaldehyde was converted into benzaldehyde in the absence of $NaHCO_3$. Benzaldehyde (18%) was given with the addition of H_2O_2 and $NaHCO_3$, and the addition of chitosan could not significantly enhance the catalytic performance. The above results showed that synergistic action between β-CD and the functional group of chitosan played a crucial role for the oxidation of cinnamaldehyde. β-CD–CTS exhibits much better catalytic ability than that of β-CD, which indicates that the support associated with β-CD has a significant positive influence for the reaction system owing to the intermolecular weak interactions, e.g. hydrogen bond between cinnamaldehyde and β-CD–CTS.

2.2.2 *Effect of β-CD–CTS amount*

The effect of β-CD–CTS amount on the oxidation of cinnamaldehyde was also investigated by varying its amount from 0 to 0.20 g, as shown in Table 1. The results indicated that the conversion of cinnamaldehyde and yield of benzaldehyde increased with an increase in the catalytic amount, coupling with a slight enhancement of selectivity for benzaldehyde. Maximal conversion (ca. 99%) was obtained with 0.10 g of catalyst. It should be noted that the oxidation reaction in aqueous solution at 60°C for 2.5 h gave 78% yield of benzaldehyde, which is significantly higher than that of the previous report (63%) (*16*), indicating that β-CD–CTS can significantly improve the yield of benzaldehyde than that from the oxidation of cinnamaldehyde with β-CDP as the phase-transfer catalyst. On the other hand, excessive β-CD–CTS would lead to unwanted side reactions and cause decrease in benzaldehyde yield. It could be ascribed to further oxidation of benzaldehyde into benzoic acid catalysed by the excess amount of β-CD–CTS.

2.2.3 *Effect of reaction temperature*

The effect of reaction temperature on the oxidation of cinnamaldehyde catalysed by β-CD–CTS is shown in Figure 7. The temperature range of 30–70°C has been studied. The results indicated that the rising temperature could improve the conversion of cinnamaldehyde and the yield of benzaldehyde significantly, suggesting that the reaction was highly sensitive to the temperature. Cinnamaldehyde conversion (96%) and benzaldehyde yield (78%) were obtained at 60°C. However, when the temperature was over 60°C, the yield would decrease resulting in the polymerisation and disproportionative condensation of benzaldehyde (*24*). In addition, lower temperature is especially advantageous for keeping the natural essence of benzaldehyde. Thus, the optimal temperature for the oxidation of cinnamaldehyde to benzaldehyde is 60°C.

2.2.4 *Effect of the amount of H_2O_2*

Hydrogen peroxide, with high active oxygen content, is an environmentally friendly oxidant for which water is the sole by-product (*25*). The amount of H_2O_2 used in this system is another important factor influencing the oxidation of cinnamaldehyde. The H_2O_2 amount from 0 to 5 ml was investigated, as shown in Table 2. The conversion increased with an increase in H_2O_2 amount. In the absence of H_2O_2, only 17% conversion of cinnamaldehyde and 9% yield of benzaldehyde were obtained due

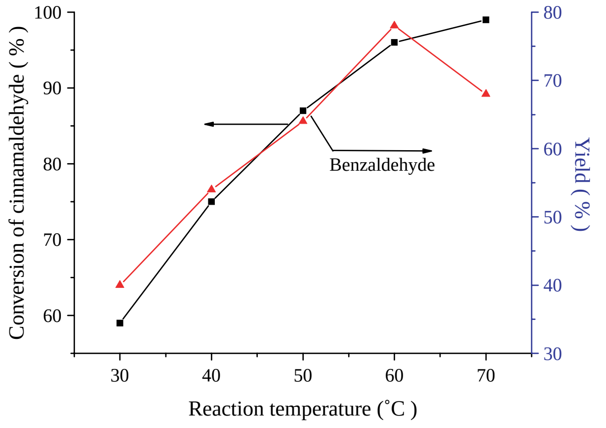


Figure 7. Effect of reaction temperature on cinnamaldehyde oxidation: 1 mmol cinnamaldehyde, 0.1 g β-CD–CTS, 4 ml H_2O_2 (w/w), 2.5 mmol $NaHCO_3$, 25 ml H_2O, 2.5 h.

Table 2. Effect of the amount of H_2O_2 on the oxidation of cinnamaldehyde.[a]

Entry	Amount of H_2O_2 (ml)	Conversion of cinnamaldehyde (%)	Yield of benzaldehyde (%)	Yield of epoxide (%)	Yield of phenylacetaldehyde (%)
1	0	17	9	0	0
2	1	70	51	13	3
3	2	80	61	10	4
4	2 + 1	88	70	6	5
5	2 + 2	96	78	2	6
6	2 + 2 + 1	93	71	2	5

[a] Reaction conditions: 1 mmol cinnamaldehyde, 0.10 g β-CD–CTS, 2.5 mmol $NaHCO_3$, 25 ml H_2O, 60°C, 2.5 h.

Table 3. Effect of the different amounts of $NaHCO_3$ on the oxidation of cinnamaldehyde.[a]

Entry	$NaHCO_3$ (mmol)	Reaction time (h)	Conversion of cinnamaldehyde (%)	Yield of benzaldehyde (%)	Yield of epoxide (%)	Yield of phenylacetaldehyde (%)
1	0	4	5	4	0	0
2	0.5	3	70	51	15	2
3	1.5	2.5	81	62	13	5
4	2.0	2.5	90	72	10	6
5	2.5	2.5	96	78	2	5
6	3.5	2	99	70	2	5

[a] Reaction conditions: 1 mmol cinnamaldehyde, 0.10 g β-CD–CTS, 4 ml 30% H_2O_2 (w/w) 2.5 mmol $NaHCO_3$, 25 ml H_2O, 60°C.

to hydrolysis of cinnamaldehyde catalysed by bicarbonate, also indicating that alkaline hydrolysis via retro-Aldol condensation is not predominant in the present reaction system. Conversion of cinnamaldehyde (96%) and yield of benzaldehyde (78%) were obtained when the amount of H_2O_2 reached 4 ml. Further increase in H_2O_2 amount did not improve the conversion.

2.2.5 *Effect of the amount of $NaHCO_3$*

Hydrogen peroxide is a weak oxidant in the absence of activators. According to the previous reports (*26*, *27*), the bicarbonate–H_2O_2 system was a simple and efficient method for the activation of hydrogen peroxide. The effect of the amount of sodium bicarbonate from 0 to 3.5 mmol on the oxidation of cinnamaldehyde is summarised in Table 3. The result indicated that the amount of $NaHCO_3$ plays an important role for the oxidation of cinnamaldehyde. In the absence of $NaHCO_3$, the conversion of cinnamaldehyde and the yield of benzaldehyde were only 5% and 4%, respectively. With an increase in the $NaHCO_3$ amount, the conversion of cinnamaldehyde and the yield of benzaldehyde increased significantly. Yield of benzaldehyde (78%) was obtained when the amount of $NaHCO_3$ reached 2.5 mmol. As previously reported (*26*), it has been confirmed that a key aspect of such reactions is that hydrogen peroxide and bicarbonate combine in an equilibrium process to produce peroxymonocarbonate ($HOOCO_2^-$). Peroxymonocarbonate is an active oxidant, which efficiently promotes the epoxidation of cinnamaldehyde, which is further oxidised to benzaldehyde. Similarly, excessive $NaHCO_3$ would decrease the yield of benzaldehyde due to increase in side reactions.

2.3 *Kinetic studies*

The oxidation rate of cinnamaldehyde in the presence of β-CD–CTS is represented in Figure 8(A). Linear relationship between $\ln(C_0/C_t)$ and time was observed, indicating that the reactions followed pseudo-first-order kinetics:

$$\ln(C_0/C_t) = kt. \tag{1}$$

Here, C_0, C_t, t and k are the initial cinnamaldehyde concentration, cinnamaldehyde concentration at t, reaction

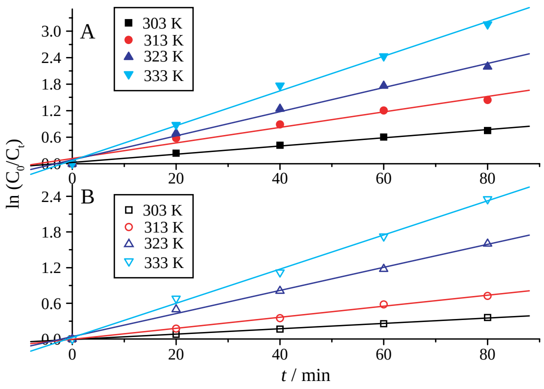


Figure 8. Pseudo-first-order plots of cinnamaldehyde oxidation by H_2O_2–$NaHCO_3$ system at different reaction temperatures in the presence and absence of β-CD–CTS.

Table 4. The rate orders and rate constants at different reaction temperatures in the presence and absence of β-CD–CTS.

	Presence of β-CD–CTS		Absence of β-CD–CTS	
T (K)	k (min^{-1})	Correlation coefficient (R)	k (min^{-1})	Correlation coefficient (R)
303	0.00931	0.9964	0.00451	0.9986
313	0.01756	0.9979	0.00927	0.9991
323	0.02729	0.9951	0.01941	0.9976
333	0.03930	0.9980	0.02875	0.9983

time (min) and the globe reaction apparent rate (min^{-1}), respectively. The slope of $\ln(C_0/C_t)$ versus t was used to calculate k.

The rate constant k (min^{-1}) and correlation coefficient R of oxidation process are shown in Table 4. The rate constant of pseudo-first-order kinetics increases with rising reaction temperature. The rate constant was found to increase from 0.00931 to 0.03930 min^{-1} when the temperature increased from 303 to 333 K.

Figure 8(B) shows the fitting results of the first-order kinetic model, which also indicated that the oxidation of cinnamaldehyde to benzaldehyde in the absence of β-CD–CTS followed pseudo-first-order kinetic model. The corresponding parameters are shown in Table 4. The rate constant increased from 0.00451 to 0.02875 min^{-1} with the temperature rise from 303 to 333 K.

As shown above, the rate constants in the presence of β-CD–CTS were higher than those without β-CD–CTS, suggesting that β-CD–CTS could significantly promote the oxidation of cinnamaldehyde. The relationship between rate constant and the temperature can be described by:

$$k = k_0 \exp(-E_a/RT). \quad (2)$$

Here, k is the rate constant of reaction (min^{-1}), k_0 is the constant-frequency factor (min^{-1}), E is the activation energy of the reaction ($\mathrm{kJ\,mol}^{-1}$), R is the gas constant ($8.314\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$) and T is the absolute temperature (K).

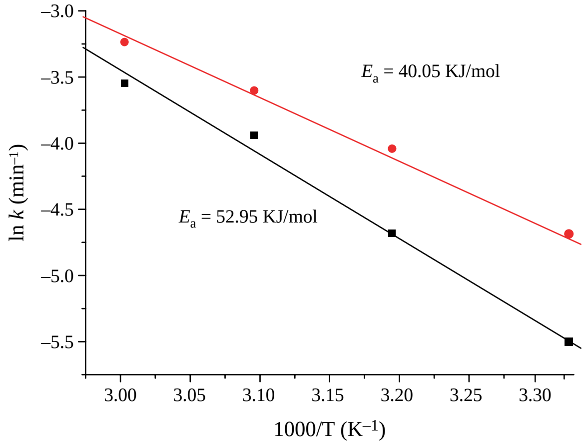


Figure 9. Arrhenius plots of the rate constants for cinnamaldehyde oxidation. (●: in the presence of β-CD–CTS; ■: in the absence of β-CD–CTS).

According to the rate constants in Table 4, Arrhenius plots of ln k and $1/T$ are shown in Figure 9. The activation energies E_a in the presence and absence of β-CD–CTS were calculated as 40.05 and 52.95 $\mathrm{kJ\,mol}^{-1}$, respectively. It is obvious that β-CD–CTS could reduce the energy barrier for the oxidation of cinnamaldehyde.

2.4 *Reusability of catalyst*

The insoluble β-CD–CTS could be easily recycled by centrifugation after the reaction. The filtered β-CD–CTS was washed with ethanol and deionised water. After drying, the catalyst was reused for the next run under the same conditions. As shown in Table 5, similar conversion and selectivity were obtained when the recovered β-CD–CTS was reused for four times. The catalytic activity was not affected.

2.5 *Effect of hydrogen bonds*

2.5.1 *FT-IR analysis of the inclusion complex*

The IR spectra of β-CD–CTS (a), physical mixture of β-CD–CTS and cinnamaldehyde (b), β-CD–CTS–cinnamaldehyde complex (c) and cinnamaldehyde (d) were recorded from 400 to 4000 cm^{-1}, as shown in Figure 10. The spectra of physical mixture (b) and inclusion complex (c) are similar to that of β-CD–CTS (a), indicating that the main structure between the inclusion complex or physical mixture and β-CD–CTS is the same. The characteristic peaks of β-CD–CTS (a) and cinnamaldehyde (d) were

Table 5. Reusability of β-CD–CTS for the oxidation of cinnamaldehyde.[a]

Entry	β-CD–CTS	Conversion (%)	Selectivity (%)
1	Fresh	96	81
2	Reuse 1	95	79
3	Reuse 2	94	78
4	Reuse 3	94	79
5	Reuse 4	93	78

[a] Reaction conditions: cinnamaldehyde (1 mmol), β-CD–CTS (0.10 g), 30% H_2O_2 (4 ml, w/w), $NaHCO_3$ (2.5 mmol), H_2O (25 ml), 60°C, 2.5 h.

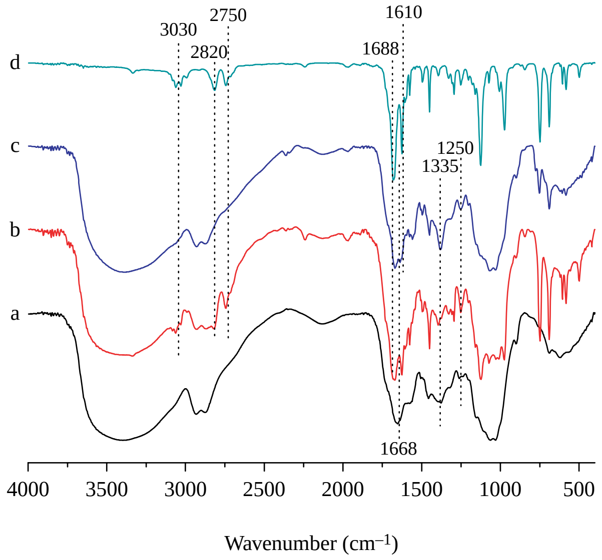


Figure 10. FT-IR spectra of β-CD–CTS (a), physical mixture of β-CD–CTS and cinnamaldehyde (b), β-CD–CTS–cinnamaldehyde (c) and cinnamaldehyde (d).

observed at the same position for the physical mixture. However, for the spectrum of inclusion complex (c), obvious difference of characteristic absorption peaks for benzene ring of the guest could be found: (1) $\sigma_{C=C}$ peak (1610 cm^{-1}) vanished; (2) the intensity of $\sigma_{C=O}$ peak (1688 cm^{-1}) decreased and shifted to 1668 cm^{-1} for the inclusion complex. These changes indicate that the aromatic part in cinnamaldehyde was included into the hydrophobic cavity of β-CD–CTS. (3) σ_{C-O-H} peaks at 1335 and 1250 cm^{-1} for the inclusion complex have much higher intensity compared to that of β-CD–CTS. These evidences indicate the formation of hydrogen bonds between the hydroxyl groups of β-CD–CTS and the carbonyl groups of cinnamaldehyde. (4) σ_{C-H} (3030 cm^{-1}) in the benzene ring and σ_{C-H} at the 2820 and 2750 cm^{-1} in the aldehyde group for cinnamaldehyde disappeared in the IR spectrum of the inclusion complex. This is probably attributed to the fact that cinnamaldehyde enters into the cavity of β-CD–CTS as well, respectively. Based on the above discussion, it is reasonable to conclude that the host–guest inclusion complex was formed (*28*).

2.5.2 *X-ray photoelectron spectroscopy (XPS) analysis of the inclusion complex*

In order to explore the high selectivity of β-CD–CTS catalyst, the difference in binding energy (BE) of β-CD–CTS before and after cinnamaldehyde inclusion was investigated and evaluated by XPS. The corresponding spectra of N1s, C1s and O1s are shown in Figure 11. Comparing the binding energies of each element between β-CD–CTS and the inclusion complex, the C1s BE of C—NH_2 was shifted to 285.8 eV from 285.3 eV, while the shift of the other C1s BEs of C—C (or C—H), C—O and C═O (or O—C—O) was not obvious (Figure 11(e)). The N1s BEs further evidenced the change, and the N1s BE of NH_2—C in the inclusion complex shifted from 402.2 to 401.6 eV (Figure 11(d)). Moreover, new peaks at 398.8 and 533.8 eV were detected, which should be assigned to the N1s BE of N—H···O and the O1s BE of O—H···O group in the inclusion complex, respectively. The results showed that the C1s BE of C—NH_2 increased and that the N1s BE of β-CD–CTS decreased after inclusion of cinnamaldehyde. It could be attributed to the formation of hydrogen bond between C═O of cinnamaldehyde and OH or NH_2 groups of β-CD–CTS, respectively. Therefore, the changes of O1s of C═O indicate the formation of hydrogen bond among C═O of cinnamaldehyde, which confirms the formation of hydrogen bond in the complex.

2.5.3 *Theoretical results*

Geometries and energies of the most stable inclusion complexes of glucopyranoside unit in isolated β-CD–CTS with cinnamaldehyde or benzaldehyde optimised by the program package DMol3 method are displayed in Figure 12. The negative BEs further demonstrate that glucopyranoside unit in the isolated β-CD–CTS can interact with cinnamaldehyde or benzaldehyde to form stable inclusion complexes. For the hydrogen bond interaction of O—H···O, as previously reported (*29*, *30*), the cut-off criteria of hydrogen bond interaction are the O···O distance from O—H···O hydrogen bond (≤3.2 Å) and the bond angle (≥90°). The bond lengths of hydrogen bonds of O—H···O (a) and (b) are in turn 2.457 and 2.728 Å, and the corresponding bond angles are in turn 110.539° and 131.908°, demonstrating that the hydrogen bond between cinnamaldehyde or benzaldehyde and the isolated β-CD–CTS plays a vital role in the reaction processes. Hydrogen bond, which leads to more cinnamaldehyde in the cavities of β-CD, effectively expands the interface and significantly promotes the oxidation of cinnamaldehyde to benzaldehyde. According to the previous report (*30*, *31*), difference between the two BEs of cinnamaldehyde and benzaldehyde is the base for selective separation of the two aldehydes in β-CD–CTS via β-CD inclusion. The more negative the BE, the more stable the corresponding β-CD–CTS/guest complex. It should be noted that different BEs lead to difference in stability between cinnamaldehyde or benzaldehyde and glucopyranoside unit in the β-CD–CTS. Herein, the BE for the glucopyranoside unit/cinnamaldehyde (−80.76 kJ/mol) is negative, which is much lower than that of the glucopyranoside unit/benzaldehyde (−47.55 kJ/mol) in the isolated β-CD–CTS. From an energetic point of view, it can be concluded that cinnamaldehyde prefers to penetrate the hydrophobic

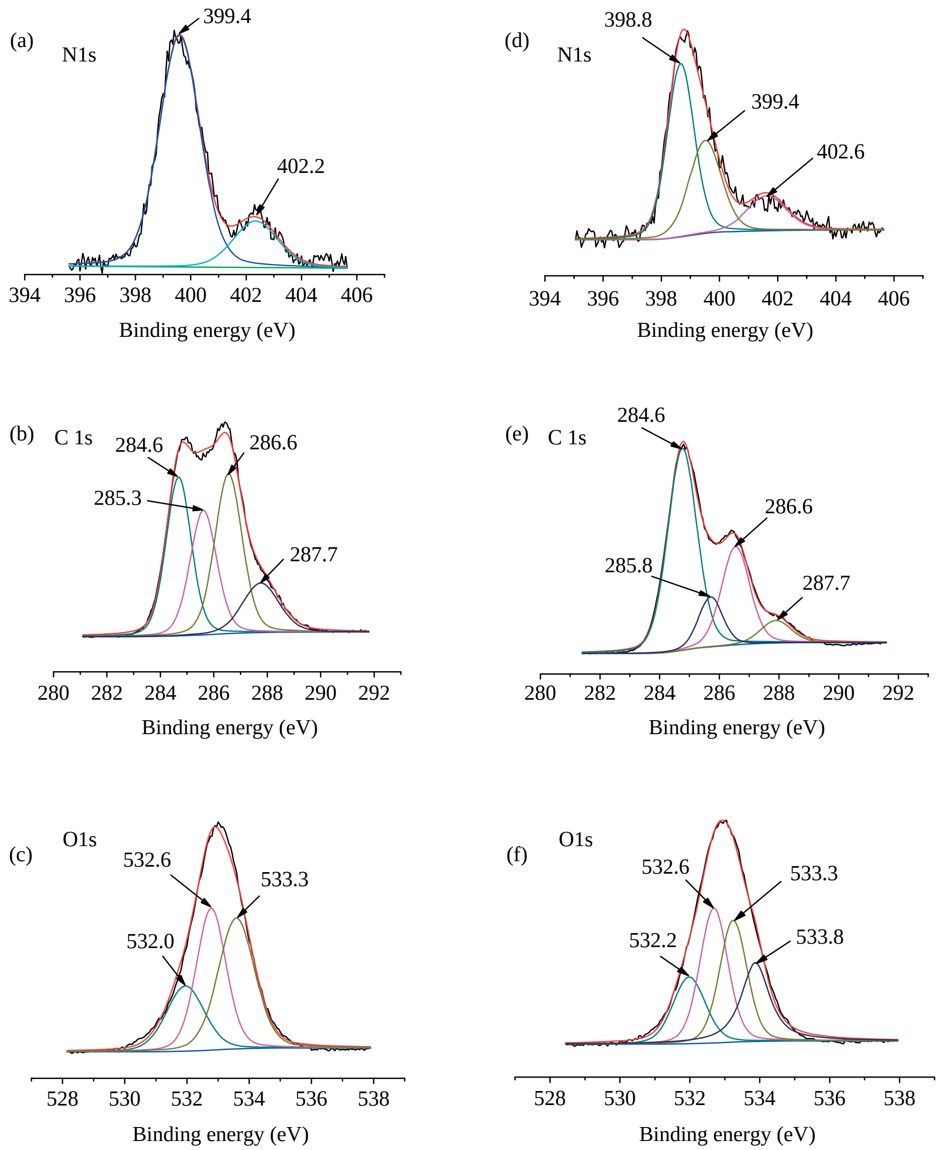


Figure 11. XPS of N(1s) (a), C(1s) (b) and O(1s) (c) core-level spectra of β-CD–CTS, and N(1s) (d), C(1s) (e) and O(1s) (f) core-level spectra of β-CD–CTS/cinnamaldehyde inclusion complex.

cavity rather than staying in the bulk of the aqueous phase. The produced benzaldehyde tends to escape the cavities of β-CD in β-CD–CTS owing to the much higher BE. Therefore, β-CD–CTS can be used to enhance the mass transfer significantly, that is why the optimal ratio (cinnamaldehyde:β-CD–CTS) is much lower than the previously reported data (1:1) (*24*). Therefore, mass transfer of β-CD–CTS significantly improves the catalytic ability.

2.6 *Plausible mechanism for the reaction*

The oxidation of cinnamaldehyde to benzaldehyde catalysed by β-CD–CTS in the presence of H_2O_2/-$NaHCO_3$ in a batch was investigated by GC–MS with naphthalene as an internal standard. The dependence of the conversion of cinnamaldehyde and the yields of the products on reaction time are shown in Figure 13. The conversion of cinnamaldehyde was greatly increased by extending the reaction time. The yield of epoxide almost simultaneously reached to 70% at the time of 0.5 h, and then gradually decreased to 2%. The yield of benzaldehyde increased to 78% at the time of 2.5 h. On the other hand, the yield of phenylacetaldehyde was obtained at the yield of 6% at the same time and kept constant despite extending the time. The above results suggest that epoxide is intermediate in the reaction process. Peroxymonocarbonate can efficiently promote epoxide to benzaldehyde in the system.

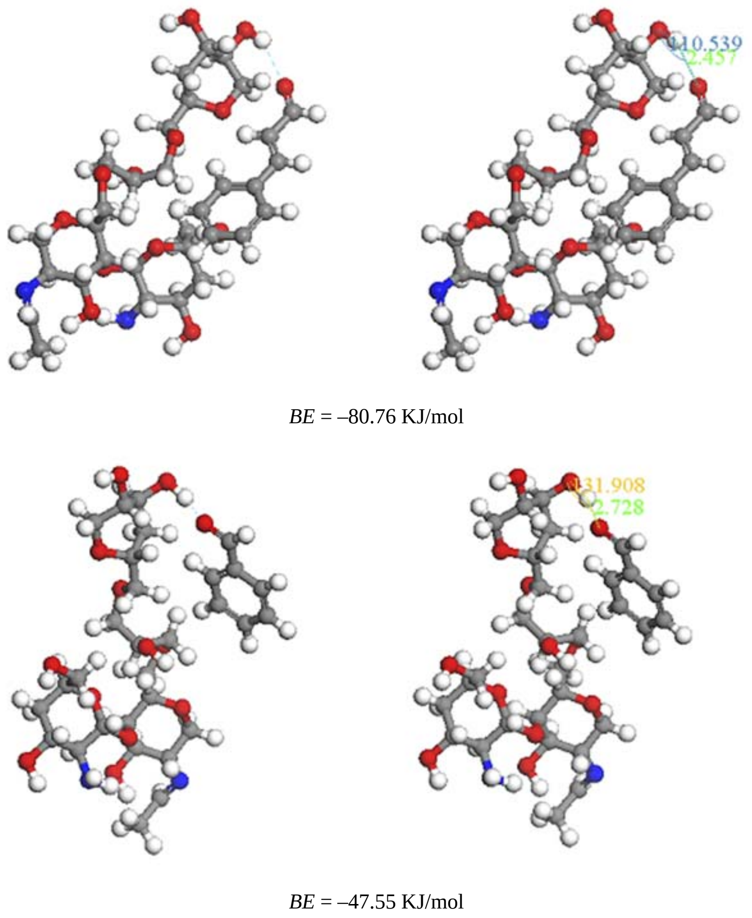


Figure 12. Optimised structure of glucopyranoside unit/cinnamaldehyde (a), glucopyranoside unit/benzaldehyde (b) in the isolated β-CD–CTS obtained by DMol3 method.

Based on the above experimental data, together with XPS and calculation results, a plausible reaction mechanism has been proposed for β-CD–CTS-catalysed oxidation of cinnamaldehyde by H_2O_2–$NaHCO_3$. Firstly, β-CD in the β-CD–CTS and cinnamaldehyde can form the inclusion complex with the intermolecular hydrogen bond O—H···O at the second rim of β-CD (Figure 14). The host–guest interaction between cinnamaldehyde and parent β-CD has been verified by ^{1}H NMR and ROESY as previously reported (*24*). Secondly, due to nucleophilic attack of hydroxide ion via the hydrolysis of sodium bicarbonate on the substrate, small amount of benzaldehyde was directly produced via hydrolysis, and the result was in accordance with the previously reported result (*24*). On the other hand, hydrogen peroxide and bicarbonate can combine in an equilibrium process to produce peroxymonocarbonate $HOOCO_2^-$. It is well known that bicarbonate–H_2O_2 system can epoxidise alkenes through the nucleophilic attack of $HOOCO_2^-$ species to the C=C double bond (*26*). The non-covalent intermolecular interaction between

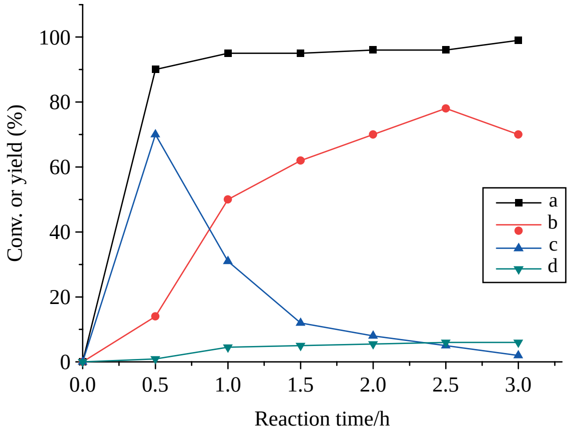


Figure 13. Plots of conversion and yields of the products versus reaction time for the cinnamaldehyde/β-CD–CTS/H_2O_2–$NaHCO_3$ system at 60°C; (a, conversion of cinnamaldehyde; b, yield of benzaldehyde; c, yield of epoxide; d, yield of phenylacetaldehyde).

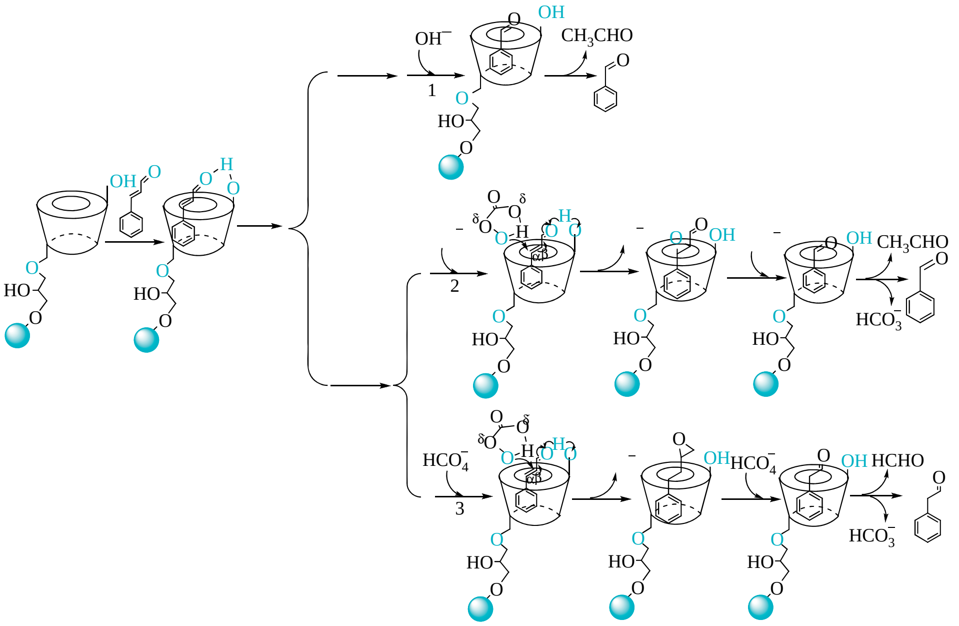


Figure 14. The plausible mechanism of the oxidation of cinnamaldehyde catalysed by β-CD–CTS in the presence of H_2O_2 and $NaHCO_3$.

β-CD and cinnamaldehyde also promoted the nucleophilic oxidation. Then, a large amount of cinnamaldehyde was converted to 3-phenyloxirane-2-carbaldehyde and a small amount of 2-phenethyloxirane was obtained in the epoxidation process, resulting from the nucleophilic attack of peroxymonocarbonate on C_α which precedes C_β in the C=C double bond. A further nucleophilic attack on the epoxide by peroxymonocarbonate produces benzaldehyde and phenylacetaldehyde, respectively. Finally, the catalyst restored its initial state. It should be mentioned that alkaline hydrolysis effect is weak in the present catalytic system, and only 9% yield of the product is derived from the contribution of hydrolysis.

2.7 *Larger scale continuous reaction experiment*

Recirculating operation of batch reaction is of interest and particularly useful in industrial-scale operation (*32*). The yield of purified benzaldehyde was up to 72% in a continuous reaction system with β-CD–CTS as the catalyst (Figure 15). Comparing with other hydrolysis of cinnamaldehyde (*24*, *33–35*), this process realises clean synthesis of natural benzaldehyde and provides excellent yield for benzaldehyde under mild conditions, which is especially important for practical application in industry. This idea of recirculating operation also gives the reference for other batch reactions.

3. Conclusions

In conclusion, the β-CD–CTS catalyst was found to be recyclable, green and extremely efficient for the synthesis of benzaldehyde from cinnamaldehyde using hydrogen peroxide as an oxidiser under mild conditions. Interaction between β-CD–CTS/cinnamaldehyde was investigated by FT-IR, XPS and computation. The results indicate that β-CD–CTS can form intermolecular weak interactions, e.g. hydrogen bond with cinnamaldehyde, then efficiently promote the oxidation of cinnamaldehyde and significantly improve the selectivity for benzaldehyde. In addition, the kinetic results show that the participation of

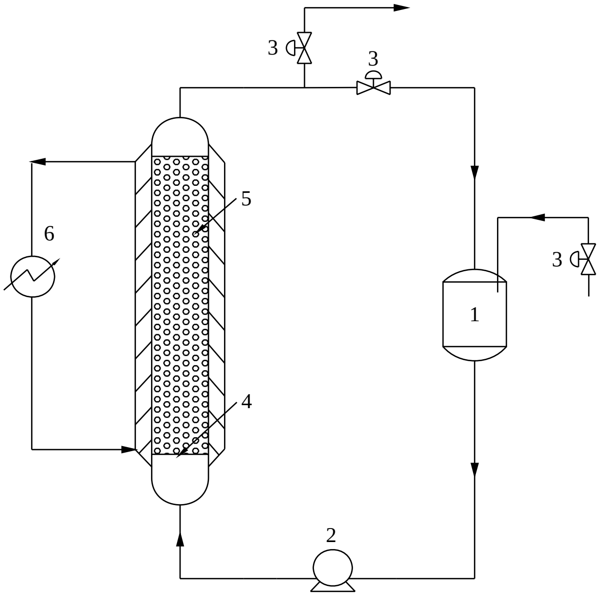


Figure 15. Apparatus for recirculating reaction system. (1) Mixing vessel; (2) pump; (3) valve; (4) sieve plate; (5) catalyst; (6) heater exchanger.

β-CD–CTS decreased the activation energy (E_a) of the oxidation, a pseudo-first-order reaction. This method is bestowed with merits such as high yield, cost effectiveness, weak alkaline aqueous phase conditions and environmentally benign nature. These advantages of the catalyst made this process very useful for the synthesis of natural benzaldehyde in industrial process.

4. Experimental

4.1 Chemicals

Chitosan with average molecular weight 50,000 and 95% deacetylation degree was obtained from Nantong Xincheng Biological Industrial Limited Co., Ltd, China. β-CD (>99%) was purchased from Shanghai Boao Biotechnology, China. Cinnamaldehyde (>99%) was obtained from Sinopharmacy Chemical Reagent, China. All other reagents and solvents were of analytical grade and used without further purification unless indicated. Distilled water was used throughout.

4.2 β-CD–CTS synthesis

Chitosan resin was prepared according to the method previously reported with some modification (*36*). A typical procedure was described as follows: 4.0 g chitosan was mechanically stirred for 30 min in 50 ml 5% aqueous acetic acid. A total of 100 ml chlorobenzene and 50 ml toluene containing 0.5 g span 80 were added in a three-necked flask. Then 7.0 g 25% glutaraldehyde was added slowly. The mixture was magnetically stirred at 40°C for 1 h and 60°C for 3 h. The reaction was stopped, and the obtained product was filtered and repeatedly washed with water–ethanol and acetone. The beads were further dried under vacuum at 60°C for 24 h.

A total of 2.0 g of chitosan resins, 50 ml of water and 50 ml of dimethyl sulphoxide were introduced into a 250 ml three-necked flask, and stirred at 25°C for 20 min. Thereafter, 0.4 mol/l sodium hydroxide was added into the reaction mixture to adjust the pH value to 10–12. The mixture was then heated to 40°C, and 45 ml of epichlorohydrin was added slowly dropwise to the solution for 90 min. The temperature was monitored during the activation and maintained for 3 h while stirring at 200 rpm. After 3 h, the mixture was filtered, and washed thoroughly with large amount of water and acetone. The product was then dried under vacuum at 40°C for 12 h.

Activated chitosan resins of 3.0 g were dispersed in 100 ml 0.2 mol/l NaOH aqueous solution with stirring. β-CD of 3.0 g was added into the reaction mixture and heated gradually to 60°C. After being stirred for 4 h at 60°C, the mixture was filtered, and washed thoroughly with large amount of water at room temperature. The product was dried under vacuum at 50°C for 24 h. The amount of β-CD immobilised on the chitosan was determined as 0.015 mmol/g according to the previously reported method (*37*).

4.3 Preparation of the inclusion complex

β-CD–CTS 0.1 g and cinnamaldehyde 0.1362 g (1 mmol) were dispersed in 25 ml deionised water. The mixture was magnetically stirred at 60°C for 0.5 h and then centrifuged. Finally, the inclusion complex was dried under vacuum at 50°C for 12 h to entirely remove the solvent, and then kept in a desiccator until used.

4.4 Characterisation of β-CD–CTS and the inclusion complex

FT-IR spectra were measured by KBr pellets. All the infrared spectra were recorded on a Bruker TENSOR 37 FT-IR spectrometer with the wavenumber ranging from 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1}. XRD patterns were measured on a Rigaku Denki MAX III diffractometer with Na-filtered Cu–Kα radiation. Step-scans were recorded for all samples in the θ range of 5°–80°. XRD peaks were analysed using the Rigaku program 'JADE-5'. TG experiments were carried out on a Netzsch STA-449C thermal analysis system. The flow rate of nitrogen was about 40 ml/min, and a heating rate of 10°C/min was used.

XPS analysis was carried out on a Vacuum Generator ESCALAB 250 spectrometer using an Al–Kα monochromatic X-ray source and a hemispherical analyser. A fixed analyser pass energy of 150 eV was used for survey scans, and high-resolution scans of core-level regions were recorded using a 20 eV pass energy. All core-level spectra were referenced to the C1s neutral carbon peak at 284.5 eV and obtained at a take-off 90° to the sample surface.

Single-contact 75.4 MHz ^{13}C CP-MAS (cross-polarisation-magic angle spinning) NMR spectra were recorded on a Bruker Avance-400 spectrometer equipped with a CP-MAS accessory. The cross-polarisation sequence was utilised for all samples, which were spun at the magic at 6 kHz. A contact time of 1 ms and a pulse (repetition) time of 5 ms were used, and more than 1000 scans were accumulated for each spectrum. The shifts were measured with respect to intensity, and approximately 300 mg of dry sample was inserted into a ceramic rotor.

4.5 Density-functional theory calculation

The inclusion complex was evaluated by the quantum-chemical calculations, since it can provide some information of BE and structure of the inclusion complex. In order to rationalise the mechanism of interaction, a basic assumption was proposed that the binding sites in the polymer are glucopyranoside unit of the β-CD in the isolated β-CD–CTS and that the global properties of these sites are not significantly different from the properties of glucopyranoside unit in the isolated β-CD–CTS molecule (as shown in Figure 16). Based on theoretical analysis, hydrophobic interactions are postulated to be the main driving forces in the inclusion complexation of cinnamaldehyde or benzaldehyde with the isolated β-CD–CTS in β-CD–CTS.

The computations were carried out using the program package DMol3 method (*38–40*) in Materials Studio (version 4.0) of Accelrys Inc. All calculations were made using the local density approximation in the Perden–Wang (PWC) form at the DND basis set level.

The BE could be expressed as

$$\mathrm{BE} = E_{\mathrm{complex}} - E_{\mathrm{guest}} - E_{\mathrm{host}}, \tag{3}$$

E_{complex} was the total energy of inclusion complex, E_{guest} was the sum of total energy of guests and E_{host} was the total energy of host. The isolated β-CD–CTS was used as host, and cinnamaldehyde or benzaldehyde was selected as model guests. The more negative the BE is, the more thermodynamically favourable is the inclusion complex.

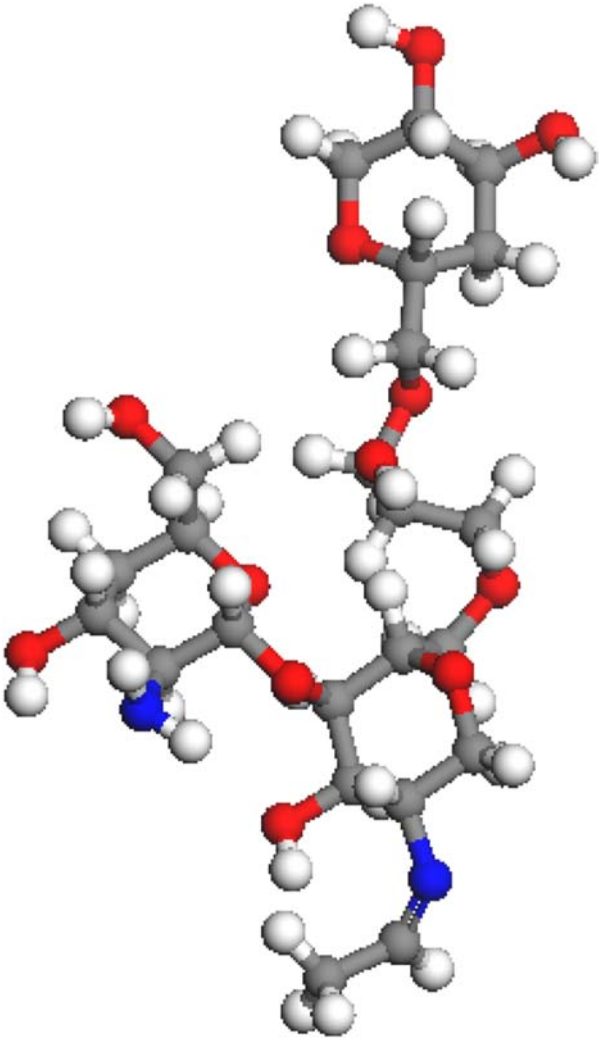


Figure 16. Optimised DMol3 isolated β-CD–CTS unit in the β-CD–CTS.

4.6 Oxidation experiments

A total of 1.0 mmol cinnamaldehyde and 2.4 mmol sodium bicarbonate were dissolved in 25 ml of deionised water at 60°C, and 0.1 g β-CD–CTS was added into a 100 ml three-necked flask fitted with a reflux condenser and magnetic stirrer. The mixture was heated to 60°C in an oil bath with electric heater, and then 4 ml 30% H_2O_2 (35.0 mmol) was added dropwise. The resulting system was performed at 60°C under stirring for 3 h. After reaction, the mixture was extracted by ethyl acetate and then centrifuged. The extracted liquid mixture was analysed by GC–MS with naphthalene as an internal standard. The reproducibility for the data was within 5%.

4.7 Kinetic experiments

Typical measurement was carried out as follows: 1.0 mmol cinnamaldehyde and 1.2 mmol sodium bicarbonate were dissolved in 100 ml of deionised water, and 0.1 g β-CD–CTS was added into a 100 ml three-necked flask fitted with a reflux condenser and magnetic stirrer. The mixture was heated and kept at 303 K (or 313, 323 and 333 K). After 30 min, 4 ml H_2O_2 (30% aqueous) was added rapidly into the mixture and the oxidation reaction occurred immediately. 0.5 ml of reaction mixture was sampled in a 1 ml pipette at 20-min intervals. The sample was diluted to 100 ml with deionised water and analysed by UV–vis at 290 nm. The UV–vis absorbance data were conversed into the product concentrations.

4.8 Large-scale experiments

The large-scale reaction experiments were carried out on a recirculating reactor. Sodium bicarbonate (24.0 mmol) was dissolved in 250 ml of deionised water, and 10.0 mmol cinnamaldehyde was dissolved in aqueous solutions in the mixing vessel. And 1 g β-CD–CTS was placed on the sieve plate of reaction equipment. The mixture was heated to 60°C in a heater exchanger, and then 40 ml of 30% H_2O_2 (350 mmol) was slowly dropped into the mixture, circling for 2.5 h at 60°C. After reaction, the solution was extracted by ethyl acetate. The extracted liquid mixture was analysed by GC–MS with naphthalene as an internal standard.

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