Oxidation-Resistant Acidic Resins Prepared by Partial Carbonization as Cocatalysts in Synthesis of Adipic Acid

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Ⓢ *Supporting Information*

ABSTRACT: The oxidation-resistant acidic resins are of great importance for the catalytic oxidation systems. In this paper, the oxidatively stable acidic resins are obtained from the cation ion exchange resins (CIERs) through the thermal treatment in N_2 atmosphere. The structure and properties of the thermally treated CIERs were characterized by chemical analysis, Fourier transform infrared (FT−IR) spectra, acid capacity measurement and scanning electron microscope (SEM). The thermally treated CIERs possess high acid capacity up to 4.09 mmol g^{-1}. A partial carbonization is observed in the thermal treatment process of CIERs, but the morphology of resin spheres maintains well. The as-prepared CIERs are used as solid acids to assist the hydrogen peroxide oxidation of cyclohexene to adipic acid (ADA) with tungstic acid as the catalyst precursor. The improved yields of ADA in the recycling reaction are obtained in the presence of acidic CIERs. Meanwhile, the unproductive decomposition of H_2O_2 is effectively suppressed. The high yields of ADA (about 81%) are kept by the thermally treated CIERs even after the fifth cycle. The thermally treated CIERs exhibit excellent acid-catalytic performance and possess remarkable oxidation-resistant capability.

KEYWORDS: *adipic acid, catalytic oxidation, oxidation-resistant resins, partial carbonization, thermal treatment*
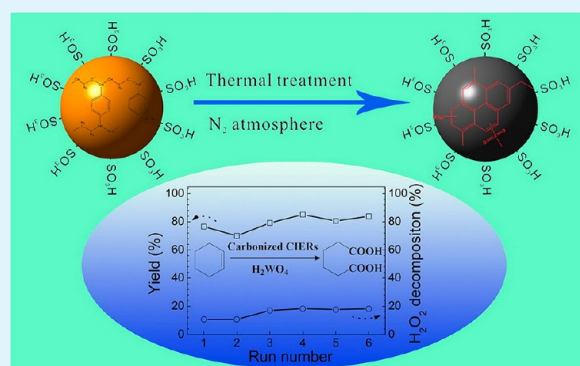
1. INTRODUCTION

In the past decades, the environmental considerations and safety concerns have been encouraging the development of solid acids. Solid acids often are used as alternatives for the hazardous and corrosive mineral liquid acids catalysts (such as sulfuric and nitric acids) in many industrial chemical processes.[1,2] As one representative class of potential solid acid materials, the acidic polymer resins often are used as Brönsted or Lewis solid acid catalysts (alone or in combination with metal ions),[3−10] supports for heterogenization of homogeneous catalysts,[11−19] precursors in the pyrolytic preparation of carbon-based catalysts and other advanced functional materials.[20−30] The cation ion exchange resins (CIERs) with high acid capacity have been extensively employed as the environmentally benign solid acid catalysts for some important reactions, such as the etherification of olefins with alcohol's, hydration, dehydration, and hydrogen peroxide oxidation reactions.[31−36] However, for their low cross-linkage and the relatively weak $CH_2−CH$ bond at the polymer chains,[37,38] the CIERs usually behave incompetent to withstand the degradation effects of the oxidative species in feed waters. Especially with hydrogen peroxide as oxidant, the CIERs become easily degradable in the oxidation reactions and no superior catalytic performance maintains for any long period use. The perfluorinated sulfonic acid resin is able to catalyze the oxidation of organic compounds efficiently with hydrogen peroxide and

also it has excellent oxidation-resistant capability and reusability, but its high cost makes the obstacle for their wide applications.[39−42] There are several methods to improve the oxidation-resistant stability of CIERs, such as improvement in the cross-linking of CIERs,[43] introduction of halogen or nitro group into the copolymers, and use of the solvents as precipitants during the polymerization process.[44] It is still a challenge to explore novel methods for the effective improvement of oxidation-resistant acidic resins.

Adipic acid (ADA) is an important bulk chemical for the production of nylon-6, 6. The direct catalytic oxidation of cyclohexene to ADA with aqueous hydrogen peroxide has been carried out over environmentally benign peroxy-tungstate-organic or inorganic complex catalysts. With its excellent yields, and organic solvent and harmful phase-transfer catalyst-free catalyst systems, this green route has become the research focus.[45,46] For this catalyst system, the acidity of organic or inorganic acid often play a key role for this oxidation reaction.[47,48] Even in the Noyori system based on Na_2WO_4, the appreciable activities and selectivity are brought about most likely by the acidic HSO_4^- in the phase transfer catalyst.[49] The acidity of

reaction system is vital for the catalysts to exhibit the excellent catalytic performances. This oxidation reaction generally involves three oxidative reactions (the epoxidation of cyclohexene, dehydrogenations of two secondary alcohols, and regio selective Baeyer−Villiger oxidation of α-hydroxy ketone) and two hydrolytic reactions,[50] in which at least two steps are facilitated by the acidic environments. Up to date, only liquid acids have been investigated to provide the acidic environments for the oxidation of cyclohexene to ADA. The liquid acids dissolve in aqueous solution with the peroxy-tungstate catalysts.

In this paper, the thermal treatment method in N_2 atmosphere was employed to obtain high stable and oxidation-resistant CIERs. The as-prepared CIERs were used as solid acid cocatalysts to assist the hydrogen peroxide oxidation of cyclohexene to ADA with tungstic acid as catalyst precursor. The superior catalytic activity and oxidation-resistant stability of CIERs were demonstrated because of the partial carbonization in the thermal treatment process.

2. EXPERIMENTAL SECTION

2.1. Preparation of Oxidation-Resistant Resin. The gel type strongly acidic CIERs was purchased from Shanghai Resin Factory Corporation. They are the three-dimensional structures of polymeric material obtained by sulfonation of a copolymer of polystrene and divinylbenzene with 7% cross-linked degree. At first, the resins were first dried at 110 °C overnight, then the dried resins (20 g, R sample) heated to different temperatures in N_2 atmosphere and kept for a constant time at those temperatures. This process was finished in a laboratory horizontal tube furnace at a heating rate of 5 °C/min. The thermal treated samples were labeled with R-X-F, "X" and "F" referred to the thermally treated temperature and thermally treated time, respectively.

2.2. Characterization of Resin Samples. Thermogravimetric (TG) and Differential scanning calorimetry (DSC) analysis were carried out in Netzsch Sta 409 PC/PG apparatus in argon atmosphere with the heating rate of 10 °C/min and in the temperature up to 800 °C. Chemical composition of resins were determined by a Flash EA 1112 elementary analyzer. The resins samples were dried at 120 °C for 12 h to measure the exact chemical compositions. The Fourier transform infrared (FT−IR) spectra of samples were recorded on a Nicolet infrared spectrometer in the wavenumber range of 4000−400 cm^{-1} at room temperature using KBr discs. The acid capacity determinations of the resins were measured according to the neutralization titration. In a typical procedure, the resins (1.5 g) dried at 110 °C for 2 h were suspended into the aqueous solution of NaOH (0.1 M, 100 mL), and then the resulting suspensions were stirred for 2 h at room temperature until the equilibrium was reached. The upper clear liquids were titrated by HCl (0.1 M) to measure the NaOH neutralized by the resins. The water contents of resins were measured by the weight method. A defined mass of the acid resin (m_1 expressed in g) were dried at 110 °C for 2 h. After being cooled down to room temperature, the dried resins were weighed (m_2 g). Water content (w%) is calculated with the formula: $w\% = (m_1 - m_2) \times 100/m_1$. The oxidation-resistant capacity of resins in hydrogen peroxide (30 wt %) was measured by a little test. The resin samples (m_3 g) dried at 110 °C for 2 h were dipped into H_2O_2 solution (30 wt %, 25 mL) in Nessler tube, then were heated at 100 °C for 3.5 h. Then residue resins were filtered out, and dried at 110 °C for 2 h, then it is weighed (m_4 g). Degradation ratio is defined as (%) = $(m_3 - m_4) \times 100/m_3$. Scanning electron microscopy (SEM) images were performed at a Hitachi S−4800 scanning microanalyser. X-ray photoelectron spectrum (XPS) were recorded on a PHI quantera SXM spectrometer with an Al $K\alpha$ = 280.00 eV excitation source, where binding energies were calibrated by referencing the C1s peak (284.8 eV) to reduce the sample charge effect.

2.3. Application in the Green Synthesis of Adipic Acid. The fresh reaction: H_2WO_4 and H_2O_2 (30 wt %) were introduced into a round-bottomed flask. The mixtures were stirred for 0.5 h to obtain

the peroxy-tungstate catalyst. Then cyclohexene was added and the system was refluxed, and then the acidic resin (the total molar ratio of H_2WO_4, cyclohexene, acid, and H_2O_2 was equal to 1:26.2:3.73:115, the acidity is imparted by the sulfonic groups in the acidic resin) was added, and the mixture was stirred at 90 °C for 6 h. The resin was separated by filtration after the reaction. The homogeneous solution was allowed to stand at 5 °C for 12 h, and then the resulting white crystal was separated by filtration and washed with cold water for three times. The product was obtained after being dried at 50 °C in vacuum overnight.

The cycle reaction: The resins can be separated from the solution by filtration process, and being washed with deionized water for three times for recycle test. The peroxy-tungstate catalyst was recycled and reused after condensing the filtrate to remove excess water on a rotary evaporator, then cyclohexene and H_2O_2 (30 wt %, the total molar ratio to H_2O_2 was equal to 1: 4.389) was added to this condensed filtrate; the mixture was then refluxed, and the separated resin from the last run was added and the reaction mixture was stirred at 90 °C for 6 h. The separations of resins and products were similar to the fresh reaction process.

3. RESULTS AND DISCUSSION

3.1. Characterization of Resin Spheres. For effective partial carbonization, an appropriate temperature range for thermal treatment will be necessary. Thermal analysis was carried out to find the appropriate temperature range for the thermal treatment to maintain the stable chemical structure of the strong acidic CIERs. TG−DSC curves of the CIERs heated under argon atmosphere are shown in Figure 1. The TG curve
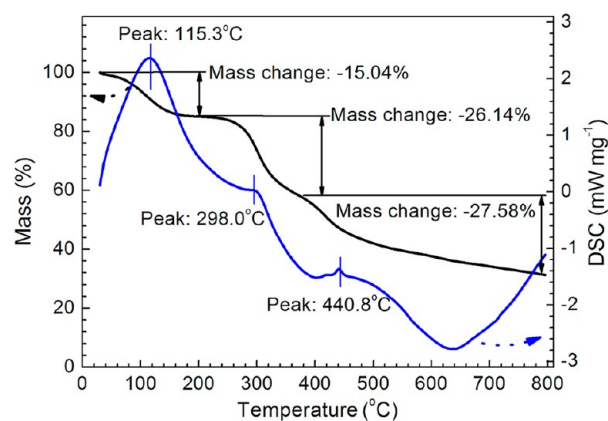

Figure 1. TG−DSC curves of the gel type strong acidic CIERs under argon atmosphere.

of CIERs exhibits three main mass loss steps in the temperature range from room temperature to 800 °C. The first weight decrease of 15.04% from room temperature to 160 °C, accompanied with an endothermic peak at about 115 °C in DSC curve, should be attributed to the dehydration of CIERs. The second decrease of 26.14% occurred in the range of 265−360 °C corresponds to the depolymerization of polystyrene-divinylbenzene structures in the resin and the desulfonation.[51,52] The last weight decrease of up to 27.58% above 390 °C should be attributed to the degradation of polystyrene and divinylbenzene structures, which destroy the chemical structures of resins completely.[53] Consequently, an appropriate temperature range from 180 to 300 °C is selected to carry out the thermal treatment in the following study.

The chemical compositions of the resin spheres thermally treated at different temperatures and for different time were investigated by the elemental analysis (Table 1). These results

Table 1. Composition, Acid Capacity, and Water Content of the CIERs Thermally Treated under Various Conditions

sample	C (%)	H (%)	S (%)	acid capacity (mmol g^{-1})	water content (%)
R	45.5	5.82	14.8	4.88	52.9
R-180 °C-1 h	47.0	6.00	15.1	4.91	50.5
R-200 °C-1 h	47.7	5.82	14.6	4.63	43.3
R-250 °C-1 h	74.1	4.83	8.48	0.39	11.4
R-300 °C-1 h	82.1	4.24	7.51	0	2.2
R-200 °C-1.5 h	48.7	5.82	14.1	4.11	35.4
R-200 °C-2 h	49.8	5.91	14.6	4.09	33.5

suggest that the thermal treatments at various temperatures have significant influences on the chemical compositions of the CIERs. The rapidly decreasing sulfur and hydrogen contents as well as the sharply increasing carbon contents at 250 °C indicate that the desulfonation and carbonization concur distinctly for CIERs. Therefore, the thermal treatments must be carried out below 250 °C to obtain the high acid capacity and the stable chemical structure of CIERs. In addition, only slightly chemical composition changes are found for the resin spheres thermally treated at 200 °C for different time. Thus, the optimal thermal treatment for the chemical stable CIERs should be obtained around 200 °C. Table 1 also presents the acid capacity and water content of the CIERs thermally treated at designed temperature and for designed time. In comparison with R sample, the acid capacity and water content decrease obviously with the increasing thermal treatment temperature, especially when the temperature is above 250 °C, indicating a desulfonation and shrinkage process for the CIERs. A long thermal treatment time have only slight effects on the acid capacity and water content. According to the results from Table 1, about 3% structural carbon proceed carbonization in R-200 °C-2 h sample.

Figure 2 represents FT−IR spectra of the CIERs thermally treated at different temperatures and for different time. In the
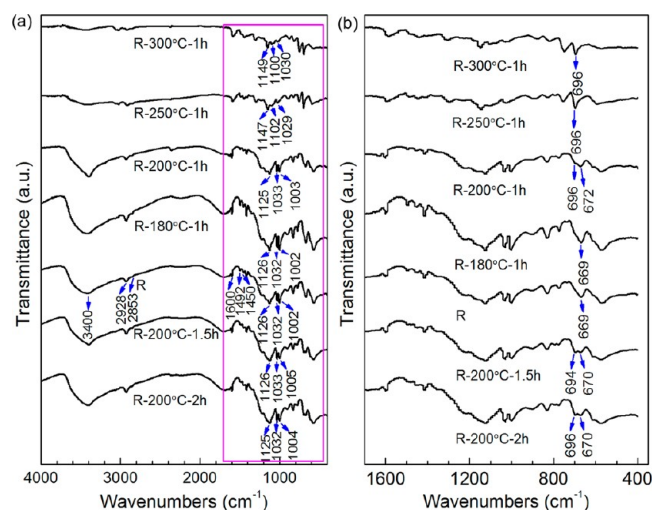

Figure 2. (a) FT−IR spectra of the CIERs thermally treated at various conditions and (b) the magnified version of the purple rectangle in a.

case of R sample, the broad absorbance band around 3400 cm^{-1} should be attributed to the stretching vibrations of adsorbed H$_2$O and the −OH groups of the sulfonic acids.[54] The peaks at

2930 and 2850 cm^{-1} are attributed to the asymmetric stretching vibration of CH$_2$ group.[55] The characteristic peaks of the aromatic ring structures lie at 1600, 1492, and 1450 cm^{-1}. Furthermore, it is found that the characteristic peaks appeared at 1126, 1032, and 1002 cm^{-1} are related to the S=O stretching vibrations.[56] The peak at 670 cm^{-1} is assigned to the bending vibration of C−S bond. The spectra of R-180 °C-1 h and R-200 °C-1 h are consistent with that of R sample. Compared to the spectrum of R sample, the peaks corresponding to S=O stretching vibrations shift to higher wavenumbers at 1147, 1102, and 1029 cm^{-1}, respectively, for samples thermally treated at 250 and 300 °C. In addition, the wavenumbers of bending vibration of C−S bond also shift from 670 cm^{-1} for R sample to 696 cm^{-1} for R-250 °C-1 h sample, revealing that the sulfone occurs due to the dehydroxylation of SO$_3$H.[57] For the sample treated at 200 °C for different time, only little variation in the kinds of characteristic peaks in FT−IR spectra was observed. The clear difference (seen in Figure 2b) is that the peak at 696 cm^{-1} referred to C−S of sulfone become much stronger with the thermal treatment for prolonging time. The appearance of sulfone suggest that the thermal treatment process of CIERs undergo the intermolecular cross-linking with the elimination of small molecules volatile compounds such as H$_2$O.[58]

XPS spectra of R and R-200 °C-2 h sample are shown in Figure 3. For R sample, there are four distinct peaks at 284.8, 532.5, 226.9, and 168.7 eV, which are attributed to C1s, O1s, S2s and S2p, respectively.[59−61] The XPS spectra of R-200 °C-2 h sample also give four peaks at 284.8, 532.1, 226.2, and 168.5 eV for C1s, O1s, S2s and S2p. In the Figure 3b, the C1s is divided into three Gaussian component peaks centered at 284.7, 285.3, and 286.0 eV, which are attributed to −C=C− bond (sp^2 carbon) linked to aromatic rings, −C−C− (sp^3 carbon) and −C−S− bond, respectively.[62,64] The area fraction of the first peak for C1s increases from 0.77 to 0.84 after thermal treatment. The results indicate that R-200 °C-2 h sample has undergone partial carbonization. The deconvolution peaks of S2p (seen in Figure 3d) are observed at 169.8 and 168.6 eV, respectively. The first peak appeared at 169.8 eV with peak area proportion of 0.38 is attributed to −SO$_3$H. The second peak located at 168.6 eV should be assigned to −SO$_2$−.[63] After the thermal treatment for R sample, the first peak area proportion decreases to 0.29, suggesting that the sulfone generates due to the dehydroxylation of SO$_3$H, which is consistent with the results from FT−IR spectra. The O1s (seen in Figure 3c) also is deconvoluted into two peaks at 532.0 and 533.4 eV, relating to O atoms in SO$_3$H and H$_2$O, respectively.[64,65]

Table S1 in the Supporting Information gives the surface chemical compositions of R and R-200 °C-2 h sample. After the thermal treatment, the increasing carbon content and decreasing sulfur content clearly indicate that the partial carbonization and desulfonation have been carried out for CIERS. The results are also consistent with that of chemical analysis.

The surface morphologies of the resin samples are observed under SEM images in Figure 4. As shown in Figure 4a and b, R and R-200 °C-2 h samples are almost identical with a good spherical shape and a smooth surface without clear cracks, which illustrates that the thermal treatment at 200 °C has almost no negative effect on the surface morphologies of CIERs.[66]

The oxidation-resistant ability of thermal treated CIERs was evaluated by the degradation ratio of sample heated in 30 wt %
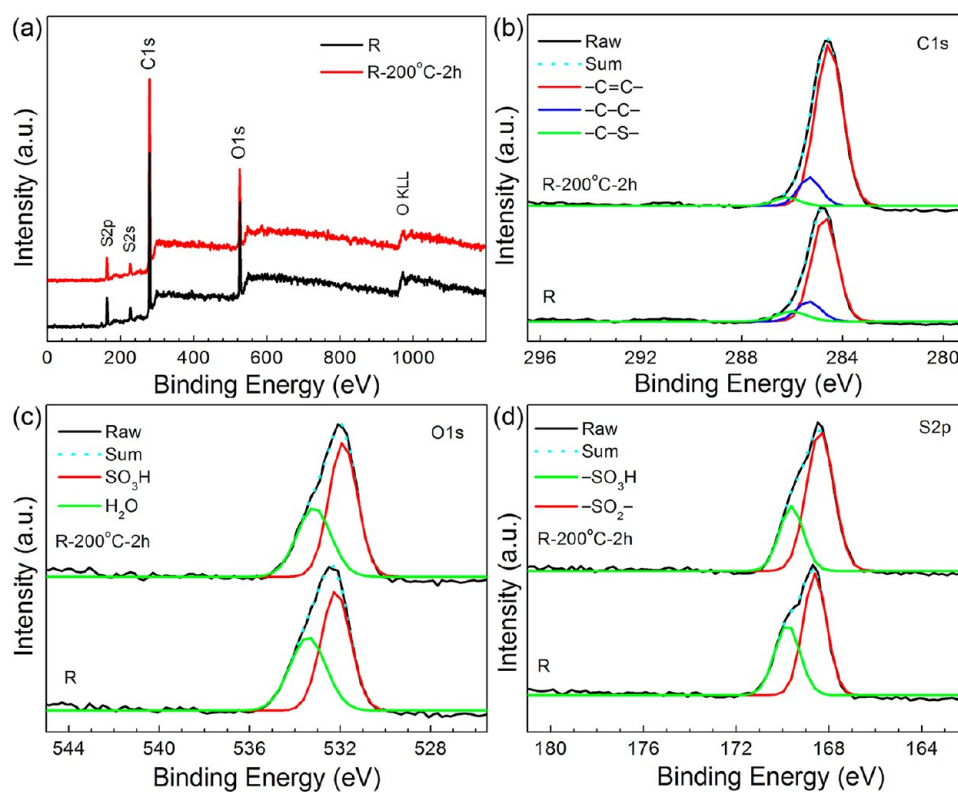
Figure 3. (a) XPS survey spectra of R and R-200 °C-2 h sample and the narrow scan of (b) C1s, (c) O1s. and (d) S2p spectra of R and R-200 °C-2 h sample.
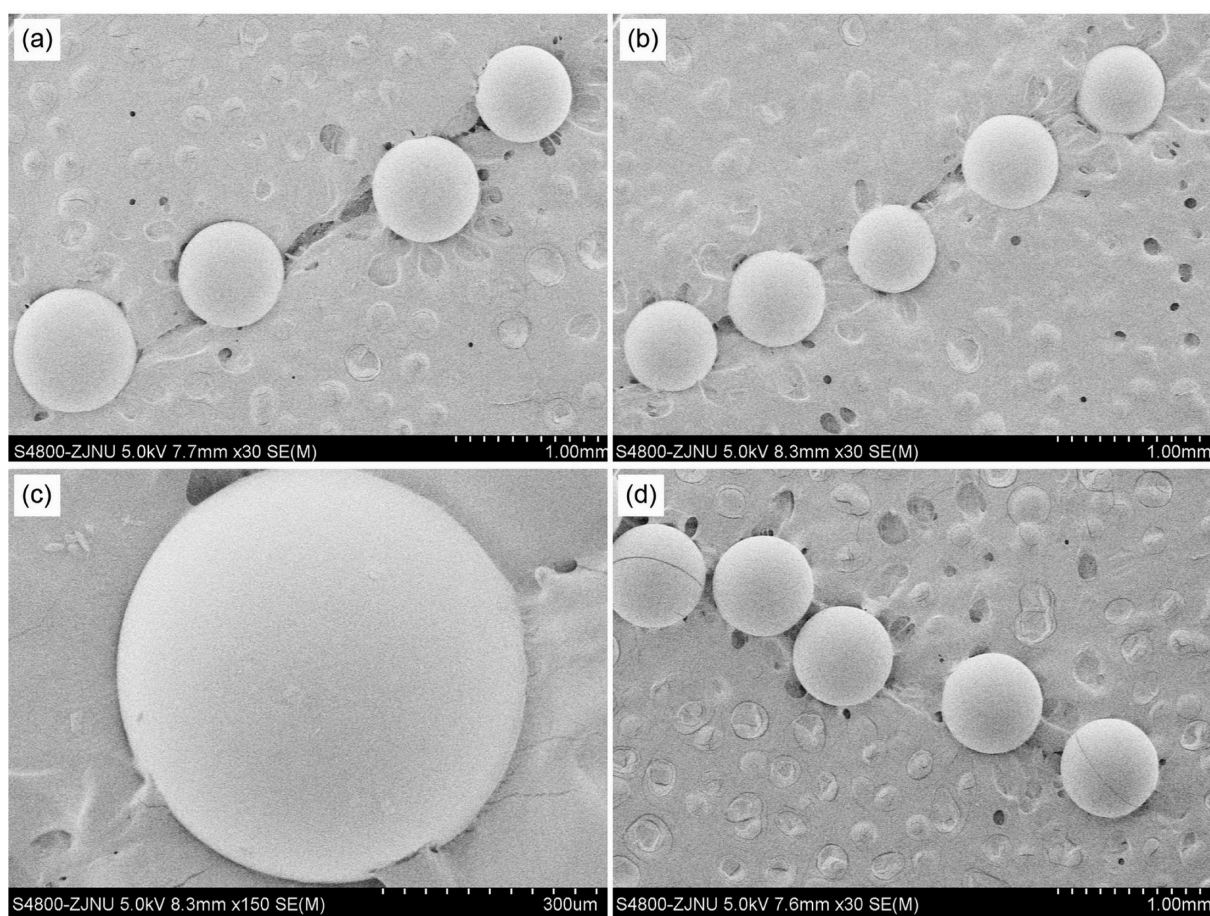

Figure 4. SEM images of (a) R, (b, c) R-200 °C-2 h, and (d) R-200 °C-2 h after the sixth reaction.
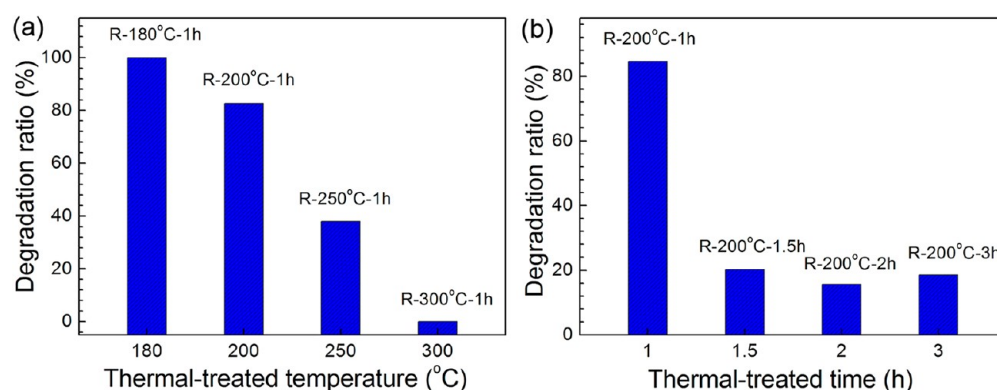
Figure 5. Degradation ratio of gel type cation exchange resins thermally treated (a) at different temperature for 1 hr and (b) at 200 °C for different times in 30 wt % H_2O_2.

hydrogen peroxide at 100 °C for 3.5 h. Degradation ratio (%) = $(m_3 - m_4) \times 100/m_3$, where m_3 and m_4 represent the weight of resin sample before and after thermal treatment in 30 wt% H_2O_2, respectively. The results were shown in Figure 5. Figure 5a presented that the influence of thermal treatment at various temperatures on the degradation ratio of the samples in aqueous 30 wt % H_2O_2. In comparison with R sample (degradation ratio: 100%), the resins sample provided obviously decreasing degradation ratio with the increase of thermal treated temperature, especially when the temperature is above 200 °C. This indicates that resins sample with the thermal treatment possess a highly improved oxidation-resistant capacity. Figure 5b shows the degradation ratio of resin samples through corresponding thermal treatment for various time at 200 °C. From Figure 5b, the thermal treatments for prolonging time remarkably enhance the oxidation-resistant capacity of resins. After the thermal treatment at 200 °C for 2 h, the resin with the best oxidation-resistant capacity is obtained, which should be attributed to the physical shrinkage and the occurrence of intrastructure rearrangement of resins, elevating the intermolecular cross-link densities.

Furthermore, the degradation ratio of 100% for macro porous resins (M sample) and macro porous resins thermally treated at 200 °C for 1.5 h (M-200 °C-1.5 h) were obtained under the identical conditions. The results reveal that the oxidation-resistant capacity of macro porous resins are inferior to CIERs. The reason may be that macro porous resins possess comparatively larger pore and higer surface area, making the resins much more accessible to hydrogen peroxide.

3.2. Application in the Green Synthesis of ADA. The specific surface area and pore volume of diried CEIRs are very small. However, CIERs will form abundant micropore in water solution. The sulfonic acid groups of CIERs will be fully dissociated in an aqueous enough environment. The acidic resin catalyst is regarded as a strong acidic aqueous solution in the presence of an inert solid polymer.[67] Therefore, three experiment groups of ADA synthesis were carried out with R sample and R-200 °C-2 h as acidic cocatalysts. The tungstic acid was used as a catalyst precursor for the direct catalytic oxidation of cyclohexene to ADA by aqueous 30 wt % H_2O_2. Every experiment group contains the fresh and three or five times cycle reactions. The reaction results are shown in Figure 6.

In this oxidation reaction, at least 4 equiv. of H_2O_2 should be provided for the complete oxidation of 1 equiv. of cyclohexene to ADA. When the unproductive decomposition ratio of H_2O_2 is higher, the oxidation would be not accomplished thoroughly due to the low oxidation capacity. Therefore the decomposition

ratio of H_2O_2 is another important parameter of catalysis valuation besides the adipic acid yield. In the absence of acidic resin (Figure 6a), the first run exhibited good ADA yield with low decomposition ratio of H_2O_2. However, with the recycling times, the yield of ADA distinctly decline and the decomposition ratio of H_2O_2 sharply rise in cycle reactions. Comparatively, the yields of ADA are higher for the oxidation reaction in the presence of acidic CIERs and particularly the unproductive decomposition ratio of H_2O_2 are much lower in fresh and cycle reactions (Figure 6b, c). These results indicate that the acidity of reaction system is the vital factor. The acidity of reaction system suppresses the decomposition ratio of H_2O_2, at the same time, it is also beneficial to maintain the activity of major catalysts. This proposed reaction pathway for this oxidation reaction (Figure 7) generally involves three oxidative reactions (epoxidation of cyclohexene, dehydrogenations of two secondary alcohols, and regio-selective Baeyer–Villiger oxidation of α-hydroxy ketone) and two hydrolytic reactions,[50] at least the hydrolytic reactions of cyclohexene oxide and adipic acid anhydride are facilitated by the acidic resin. K. Sato has also reviewed that the acidic environment is essential for the H_2O_2 involved oxidation reaction.[68] For the fresh and first two cycle reactions, the ADA yields are almost equal to each other for both pristine CIERs and thermally treated one. The ADA yields after the second cycle reaction slightly increase and maintain higher than 80% using the thermally treated CIERs (R-200 °C-2 h sample). These results demonstrate that the thermally treated CIERs exhibit high acidic catalytic performances as cocatalysts for this oxidation reaction, although the acid capacity of thermally treated CIERs is slightly lower than that of R sample. Figure 6d gives pictures of R and R-200 °C-2 h samples before and after the reactions. In comparison with 1, the apparent volume of R sample in picture 2 expands about three times more after the third cycle reaction. The resins are oxidatively degraded and dissolved in the fourth cycle reaction, while the thermally treated CIERs (R-200 °C-2 h sample) always remain integrated particles and are highly separable. The apparent volume of R-200 °C-2 h sample was almost invariable even after the fifth cycle reaction, illustrating the CIERs through thermal treatment possesses remarkably improved oxidation-resistant stability.

The FT−IR spectra (see Figure S2 in the Supporting Information) of R-200 °C-2 h sample after the sixth reaction are consistent with that of fresh R-200 °C-2 h, illustrating R-200 °C-2 h sample also possesses excellent chemical stability. The SEM images (Figure 4d) show that only some scratches formed on the surface of some CIERs particles due to the swelling
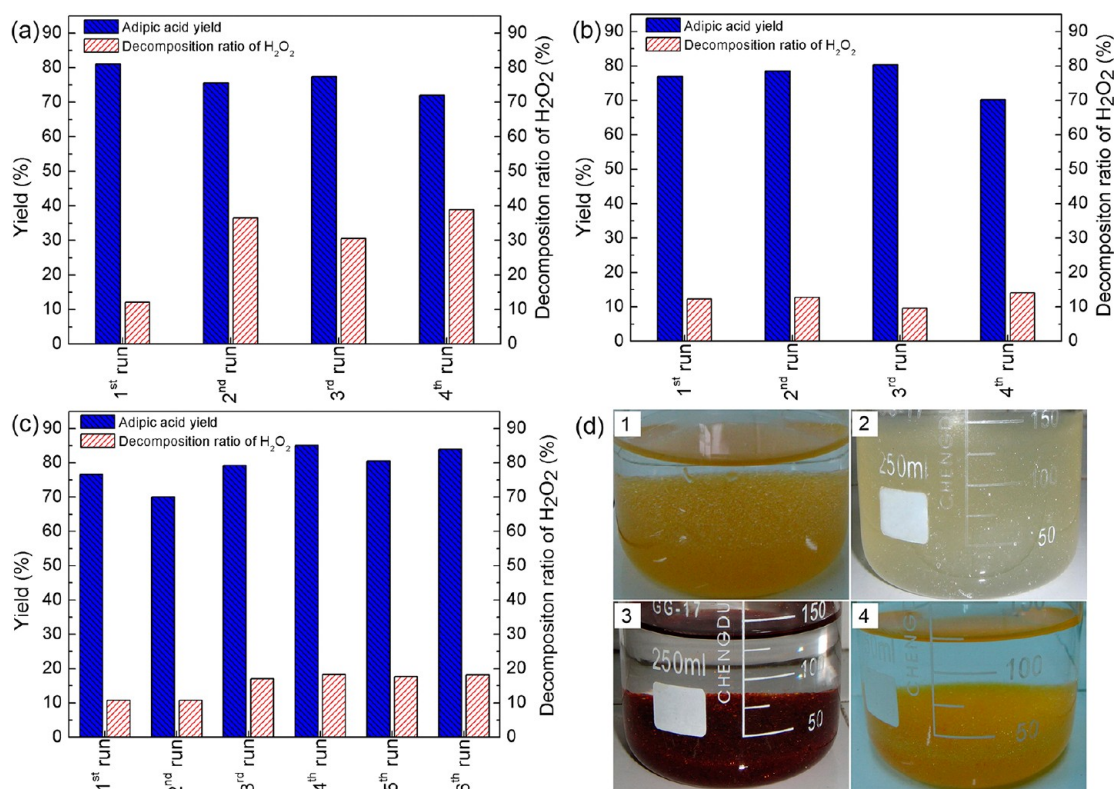
Figure 6. ADA yield and decomposition ratio of H_2O_2 in the oxidation reaction assisted by the acidic CIERs (a) without resins, (b) R sample, (c) R-200 °C-2 h sample. (d) Pictures of CIERs: (1) R sample (2) R sample after the fourth reaction, (3) R-200 °C-2 h sample, (4) 200 °C-2 h sample after the sixth reaction. The reaction solution was refluxed at 73 °C for 2 h first, then was heated to 90 °C and kept for 6 h. Decomposition ratio of H_2O_2 (%) = (the amount of unproductive decomposed $H_2O_2 \times 100$)/the total amount of H_2O_2.
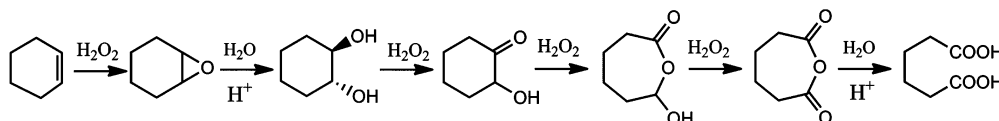

Figure 7. Proposed reaction pathway for the synthesis of adipic acid by oxidation of cyclohexene with 30 wt % hydrogen peroxide (Noyori et al.[50]).

and mechanical stirring in the reaction and their basic spherical morphologies still maintain well.

4. CONCLUSIONS

In conclusion, the oxidation-resistant resins were obtained from the gel type CIERs through the thermal treatment in N_2 atmosphere. The thermal treatment on CIERs resulted in somewhat partial carbonization of polymer resins and improved the cross-link levels of resins. The thermally treated CIERs exhibit higher oxidation-resistant capability than the raw resins in pure 30 wt % hydrogen preoxide. The excellent oxidation-resistant capability of thermally treated CIERs warrants the superior stability in the hydrogen peroxide oxidation of cyclohexene to ADA with tungstic acid as catalyst precursor. The acid capacity of the thermally treated CIERs is up to 4.09 mmol g^{-1}, which provide the important acidic environment for this catalytic reaction. The advantages of this thermal treatment and partical carbonization method manifest its attractive application potential in the hydrogen peroxide oxidation processes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Some characterization results of resin spheres. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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