

# Hierarchically Porous Hydrothermal Carbon Microspheres Supported *N*-Hydroxyphthalimide as a Green and Recyclable Catalyst for Selective Aerobic Oxidation of Alcohols

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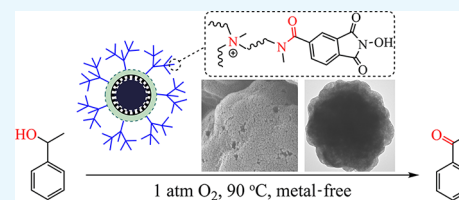


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Supporting Information

**ABSTRACT:** A novel metal-free, reusable, and green catalytic system comprising hydrothermal carbon microspheres (HCMSs) supporting *N*-hydroxyphthalimide (NHPI) was developed and employed in the aerobic oxidation of alcohol. Hierarchically porous HCMSs with good monodispersity were produced by the hydrothermal carbonization of sucrose and designed NaOH-impregnated calcination under a static air atmosphere. The meso- and macroporous pores on HCMSs make up 71% of the total pore volume. The covalent immobilization of NHPI onto HCMSs was first accomplished by grafting hyperbranched polyquaternary amine via repetitive ring-opening reactions of diglycidyl ether and subsequent amidation with 4-carboxy-NHPI. Owing to the cocatalysis of grafted quaternary ammonium salt, a designed heterogeneous catalyst has superior performance to free NHPI in the oxidation of 2-phenylethanol. The established catalytic system achieved 42% conversion and up to 96% selectivity of acetophenone at 90 °C under 1 atm O<sub>2</sub> for 20 h and presented a versatile catalytic effect for diversified alcohols. Immobilized NHPI could be facily recycled via simple filtration and displayed good stability for six cycles without a discernible decrease of reactivity or damage of catalyst morphology in repeated oxidation test.



## 1. INTRODUCTION

Selective oxidation of alcohols with molecular oxygen to valuable functional chemicals plays significant roles in organic synthesis and industrial application.<sup>1–3</sup> As powerful organocatalysts, *N*-hydroxyphthalimide (NHPI) and its derivatives have attracted increasing interest for the last few decades, in virtue of their remarkably high efficiencies in aerobic oxidation reactions.<sup>4–6</sup> Since Ishii and co-workers introduce NHPI/metallic salt systems to promote the oxidation of alkanes and alcohols with molecular oxygen, considerable progress has been made to develop many catalytic systems including the discovery of various metal-based and metal-free initiators and the synthesis of NHPI derivatives toward the oxidation of various substrates.<sup>7–13</sup> However, typical NHPI-based catalysts are generally homogeneous and are not easily recoverable after oxidation. Additionally, the work-up procedure is inconvenient and inevitably generates a lot of waste. The immobilization of NHPI onto specific solids could be attributed to two ways: non-covalent adsorption and covalent linkage.<sup>14</sup> Comparatively, NHPI supported by the non-covalent adsorption is easily achieved but has low stability and poor reusability.<sup>15,16</sup> From the view of green chemistry and economic cost, the design of high-efficiency heterogeneous catalysts utilizing shaped materials via covalent bonding is a valuable and desirable strategy.<sup>17–21</sup>

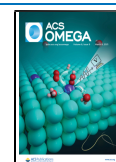
Hydrothermal carbonaceous microspheres (HCMSs) are a spherically structural material with micron size, fabricated based on the hydrothermal carbonization (HTC) of biomass

or its deriviers.<sup>22</sup> Since the first report in 2001, HCMSs have become increasingly applicable in various areas including pollutant removal, chromatographic separation, energy conversion, and storage.<sup>23–25</sup> Compared with other spherical support substrates such as silica beads and organic polymers, HCMSs can be a promising selection for a heterogeneous catalyst owing to their green synthesis, sustainable source, low cost, good chemical resistance, mechanical strength, adsorption properties, and packing performance.<sup>26–28</sup> Some works have been accomplished for the HCMS-based catalysis in the last decade. Demir-Cakan et al. prepared imidazole-modified HCMSs via the HTC of glucose using vinyl imidazole as functional monomers, which were utilized in the organocatalysis of transesterification, Knoevenagel, and Aldol reactions.<sup>29</sup> After surface modification with acid functional groups, HCMSs showed good catalytic activities for esterification, isomerization, cellulose hydrolysis, and fructose dehydration.<sup>30–33</sup> Amphiphilic HCMSs were constructed and efficiently catalyzed the solvent-free biphasic acetalization reaction.<sup>34</sup> HCMSs that immobilized various metallic nanoparticles exhibited a satisfactory catalytic effect for hydro-

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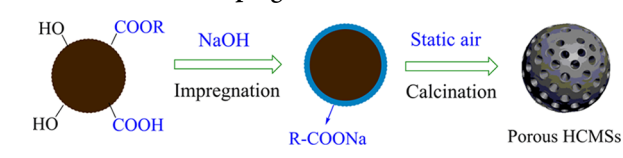
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genation of unsaturated compounds.<sup>35–38</sup> To the best of our knowledge, the HCMSs-based catalyst for aerobic oxidation of alcohols and HCMSs supporting NHPI were hardly reported.

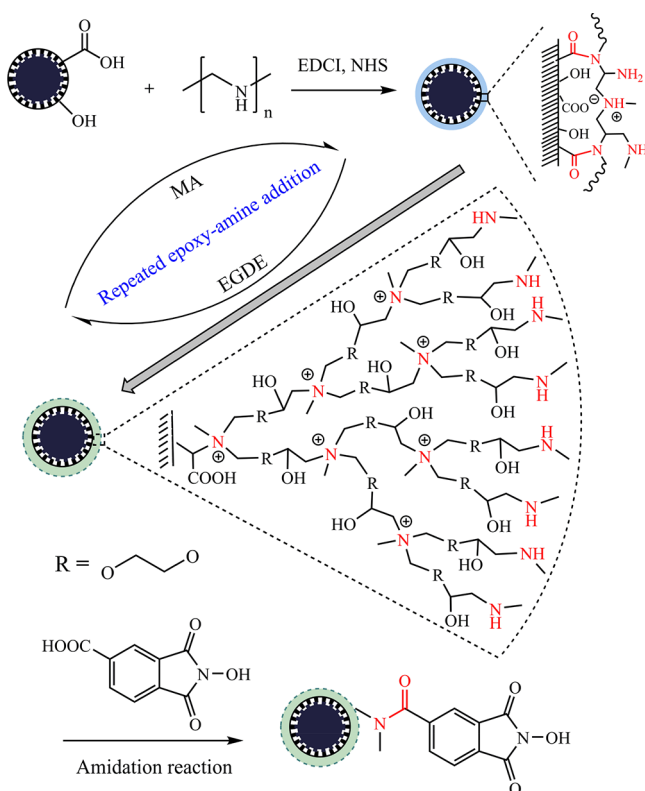
This article presents the good catalytic performance of novel NHPI-functionalized HCMSs (NHPI-HCMSs) in the aerobic oxidation of various alcohols with high stability and reusability. Conventional direct or mineral-based activation processes for HCMSs usually result in a dominantly microporous structure and/or destructed morphology,<sup>39–41</sup> which may have a negative effect on the fast and stable mass transfer during heterogeneous catalytic reaction in practice. Improving previous approaches, a NaOH-impregnated calcination under a static air atmosphere was designed to efficiently introduce plentiful meso- and macropores onto HCMSs with maintained monodispersity (Scheme 1). Considering the cocatalytic effect

**Scheme 1. NaOH-Impregnated Activation of HCMSs**



of quaternary ammonium salt in NHPI-catalytic alcohol oxidation,<sup>11,42</sup> the covalent immobilization of NHPI onto HCMSs was composed of grafting hyperbranched polyquaternary amine (HPA) and following amidation with 4-carboxy-NHPI (Scheme 2). The NHPI-HCMSs show much better catalytic conversion and selectivity in the oxidation of 1-phenylethyl alcohol (PEA) to acetophenone (AcPO) in comparison with the same amount of NHPI. This catalyst is

**Scheme 2. Illustrative Construction of NHPI-HCMSs**

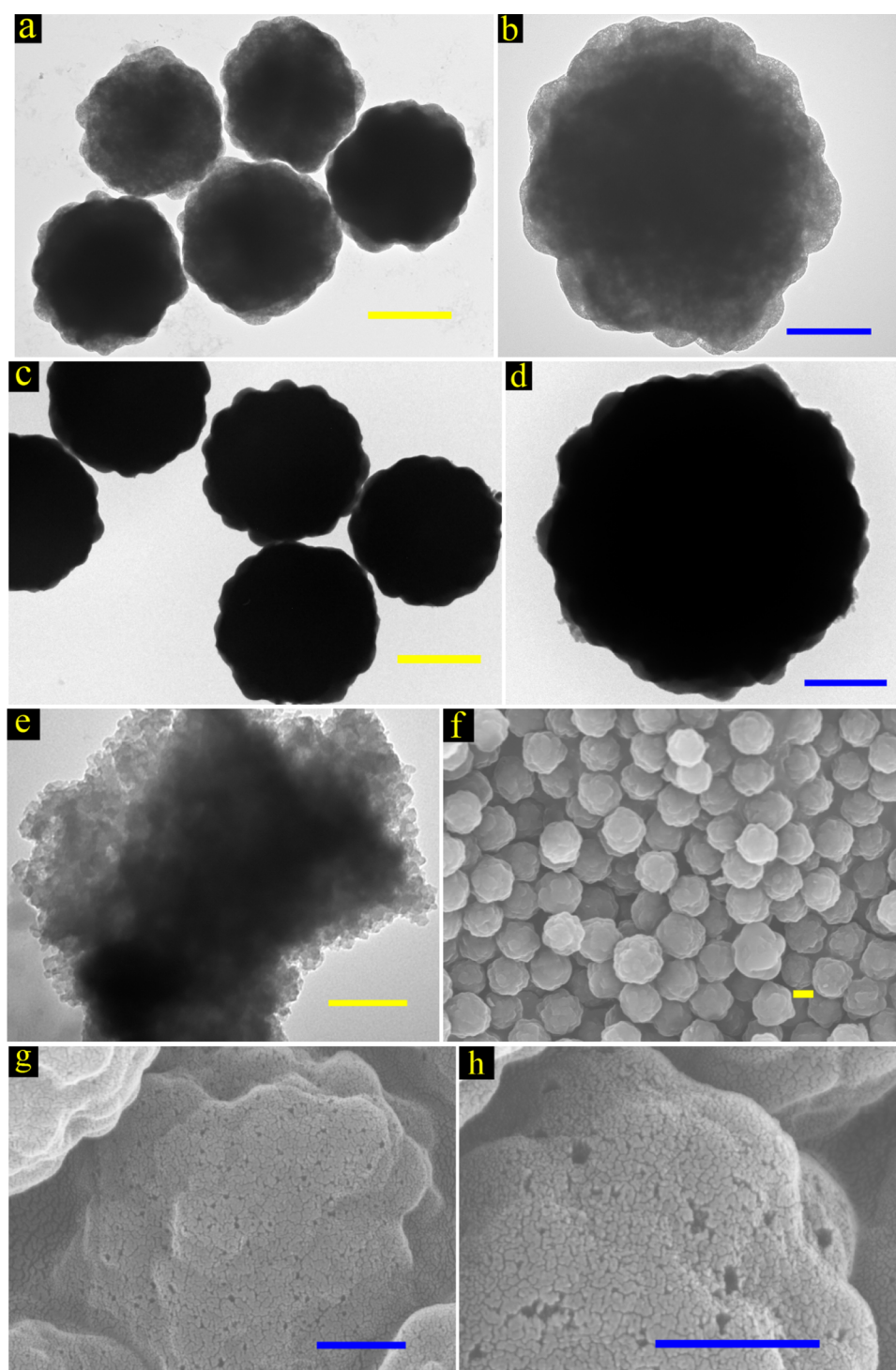


well recyclable and applicable in the oxidation of various alcohols.

## 2. RESULTS AND DISCUSSION

**2.1. Preparation of Hierarchically Porous HCMSs.** As shown in Scheme 1, the preparation of porous HCMSs is composed of two procedures: the impregnation of colloidal HCMSs obtained from the HTC of sucrose with NaOH solution and high-temperature calcinations in a static air atmosphere. After NaOH impregnation, the Fourier transform infrared (FTIR) spectra indicated that the surface carboxyl acid groups of colloidal HCMSs were transformed into alkaline sodium carboxylate (Figure S1), which were further carbonized at 850 °C in a static air atmosphere. The traditional carbonizations without NaOH and with NaOH addition were also conducted for comparison. The transmission electron microscopy (TEM) images showed the obviously richer porosity and thicker porous layer of products via NaOH-impregnated carbonization than those via carbonization without NaOH, along with both maintaining good sphericity of activated HCMSs from the above two methods (Figure 1a–d). This demonstrated the etching effect of surface sodium carboxylate in the pore-forming process of HCMSs. However, the conventional NaOH-added carbonization seriously damaged the morphology of CSs and led us to form porous irregular lumps (Figure 1e), which accord with reported literature.<sup>41,43</sup> The scanning electron microscopy (SEM) images displayed that HCMSs were well dispersed with a uniform diameter of 2.1 μm (Figure 1f), and plentiful mesoporous and macroporous structures can be clearly observed with a pore diameter ranging from 3.5 to 65 nm (Figure 1g–h). The Brunauer–Emmett–Teller (BET) test was conducted to further investigate the different porosities of HCMSs from the direct and NaOH-impregnated calcinations. There is a much more distinct H1 hysteresis loop for NaOH-impregnated HCMSs at high pressure in nitrogen adsorption–desorption isotherms (Figure 2a), which implies their better mesoporosity. Their meso- and macropore volume are detected to be 0.46 cm<sup>3</sup> g<sup>−1</sup> (71% of the total pore volume) with an average pore size of 4.9 nm in contrast with 0.21 cm<sup>3</sup> g<sup>−1</sup> (34% of the total pore volume, mean pore size: 1.5 nm) of direct-activated HCMSs (Table 1). This doubtlessly affirmed more meso- and macroporous structures on NaOH-impregnated HCMSs. The X-ray photoelectron spectroscopy (XPS) spectrum of carbon demonstrated the presence of C=O and O–C=O groups on the surface of activated HCMSs (Figure S2), which could originate from the high-temperature atmospheric oxidation.<sup>44</sup> The Boehm titration test helps determine their surface acidic groups<sup>45</sup> in which the contents of carboxyl and phenolic hydroxyl groups are detected to be 1.12 and 0.26 mmol/g, respectively. These functional groups enabled the advanced decoration of activated HCMSs.

**2.2. NHPI Functionalization.** Based on surface O–C=O groups, NHPI-HCMSs were synthesized via multiple hyperbranching quaternizations and terminal catalytic amidation with NHPI (Scheme 2). The FTIR spectrum of NHPI-HCMSs in Figure 3a exhibits significantly intensive absorption peaks at 1223, 1670, 1746, 3149, and 3385 cm<sup>−1</sup> compared with that of raw HMCs, which were derived from the stretching vibration of C–N (or C–O–C), N–C=O, C=O, aromatic C–H, and O–H groups, respectively. Some new peaks at 3002–2848 and 975–699 cm<sup>−1</sup> also appeared, corresponding to the stretching vibration of aliphatic C–H

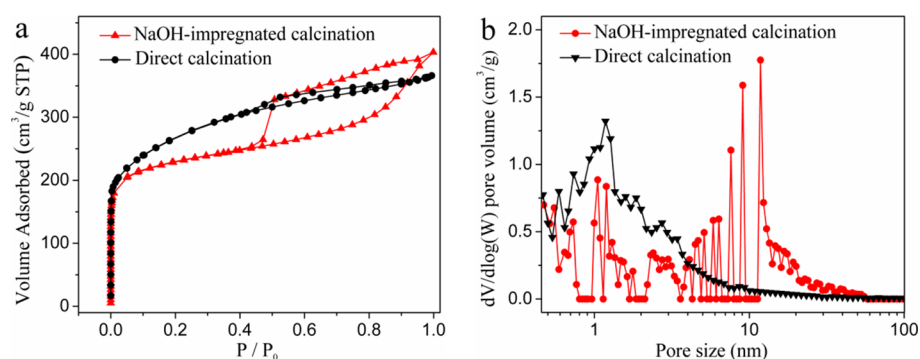


**Figure 1.** SEM and TEM characterizations (yellow bar: 1  $\mu\text{m}$ , blue bar: 500 nm). TEM (a, b) and SEM images (f–h) of HCMSs activated by NaOH-impregnated calcination; TEM images of HCMSs activated by direct calcination (c, d) and NaOH-added calcination (e).

and bending vibration of benzene rings. The elemental analysis displayed the obvious increase of the N-content from 0.11 to 5.14% (Figure 3d). The zeta potential test demonstrated the changed surface electrical property of HCMSs in water, from negative charge ( $-4.8$  eV) to positive electricity (38.7 eV) before and after modification (Figure 3d). The N1s XPS spectra further revealed apparent characteristic signals of quaternized nitrogen at 402.1 eV and neutral nitrogen (such as residual amine groups) at 398.9 eV in NHPI-HMCSs (Figure 3b). The thermogravimetric analysis (TGA) was conducted to

investigate grafted polymers on HCMSs (Figure 3c). There is only a 4.6% weight loss for raw HCMSs when the temperature increased to 700  $^{\circ}\text{C}$ , attributed to the removal of oxygen-containing groups. In comparison, the weight loss was sharply augmented to 68.3% for NHPI-HCMSs owing to the pyrolysis of hyperbranched polymers in a temperature scope of 225–540  $^{\circ}\text{C}$ . The immobilization amount of NHPI on HCMSs was detected to be 1.58  $\text{mmol g}^{-1}$  through the weight increment of HCMSs before and after the NHPI load, which corresponded with the measured result of elemental analysis (entries 2 and 3;



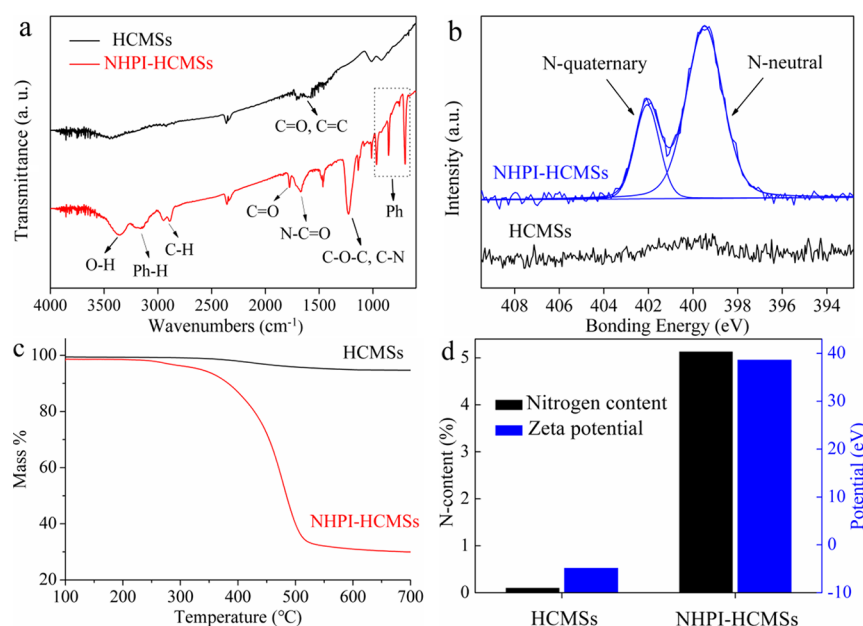


**Figure 2.** N<sub>2</sub> adsorption–desorption isotherms (a) and pore size distributions (b) of HCMSs.

**Table 1.** BET Analysis of HCMSs

entry	sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{macro\&meso}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{total}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{macro\&meso}}/V_{\text{total}}$
1	colloidal HCMSs	1.8			0.004	
2	porous HCMSs <sup>a</sup>	891	0.38	0.20	0.58	0.34
3	porous HCMSs <sup>b</sup>	677	0.19	0.46	0.65	0.71

<sup>a</sup>HCMSs were directly calcined in a static air atmosphere. <sup>b</sup>HCMSs were calcined after NaOH impregnation in a static air atmosphere.



**Figure 3.** FTIR (a), N1s XPS (b), TGA (c), N-content, and zeta potential analysis (d) of activated HCMSs and NHPI-HCMSs.

Table S1). The SEM mapping result of the nitrogen element could reflect the even distribution of modified HPA and NHPI on the surface of HCMSs (Figure S3). These facts suggested the smooth anchoring of quaternized polymers and NHPI on the surface of HCMSs.

### 2.3. Application in Catalytic Oxidation of Alcohols.

To test the catalytic properties of NHPI-HCMSs, the oxidations of PEA using molecular oxygen (1 atm) were implemented under different conditions (Table 2 and Scheme S1). The two main detected oxidative products were AcPO and 1-phenylethyl hydroperoxide (PEHP). The reaction at 90 °C for 20 h was investigated in CH<sub>3</sub>COOH at first. There was a negligible product detected in the blank experiment without the catalyst. The conversion of PEA and selectivity of AcPO were obviously increased from 16 to 42% and from 78 to 96%, respectively, with the amount of supported NHPI from 2 to 8 mol % (entries 2–4; Table 2). As the dosage augmented to 16

mol %, both the conversion and selectivity changed very little. Accordingly, 8 mol % of supported NHPI was supposed to be a desirable amount. Impressively, the same amount of NHPI only afforded 18% PEA conversion and 55% AcPO selectivity, which were markedly inferior to supported NHPI (entries 4 and 6; Table 2). Furthermore, the comparative oxidation with homogeneous NHPI and tetramethylammonium acetate also showed superior catalytic activity to that with NHPI alone (entries 6 and 7; Table 2). Therefore, the better catalytic result of NHPI-HCMSs could be rooted in the PEHP decomposition and N-hydroxyl activation promoted by quaternary ammonium salts on their surface, which has occurred in NHPI-based homogeneous catalysis.<sup>11,42,46–49</sup>

The selection of the reaction solvent, temperature, and time also mattered in the catalytic system. The effects of four common solvents used in NHPI-catalyzed reaction are presented in Table 3. Considering the low boiling temperature,

**Table 2. Oxidation of PEA Catalyzed by the Different Amounts of Catalysts<sup>a</sup>**

entry	supported NHPI (mol %)	NHPI (mol %)	conversion (%)	selectivity (%)	
				AcPO	PEHP
1	0	0	<1		
2	2	0	16	78	20
3	4	0	35	90	10
4	8	0	42	96	3
5	16	0	43	97	1
6	0	8	18	55	44
7 <sup>b</sup>	0	8	55	99	

<sup>a</sup>Reaction conditions: 10 mmol of PEA, 25 mL of CH<sub>3</sub>COOH, 1 atm O<sub>2</sub>, 90 °C, 20 h. <sup>b</sup>The oxidation result with the addition of tetramethylammonium acetate based on the same nitrogen mass with that of HPA on NHPI-HCMSs.

**Table 3. Catalytic Oxidation of PEA in Different Conditions<sup>a</sup>**

entry	solvent	time (h)	temperature (°C)	conversion (%)	selectivity (%)	
					AcPO	PEHP
1	CH <sub>3</sub> CN	20	80	22	78	20
2	PhCF <sub>3</sub>	20	90	33	83	16
3	PhCN	20	90	32	85	15
4	CH <sub>3</sub> COOH	20	80	30	91	10
5	CH <sub>3</sub> COOH	20	90	42	96	3
6	CH <sub>3</sub> COOH	20	100	43	96	2
7	CH <sub>3</sub> COOH	15	90	37	87	13
8	CH <sub>3</sub> COOH	40	90	42	97	2

<sup>a</sup>Reaction conditions: 10 mmol of PEA, 25 mL of the solvent, 8 mol % supported NHPI, 1 atm O<sub>2</sub>.

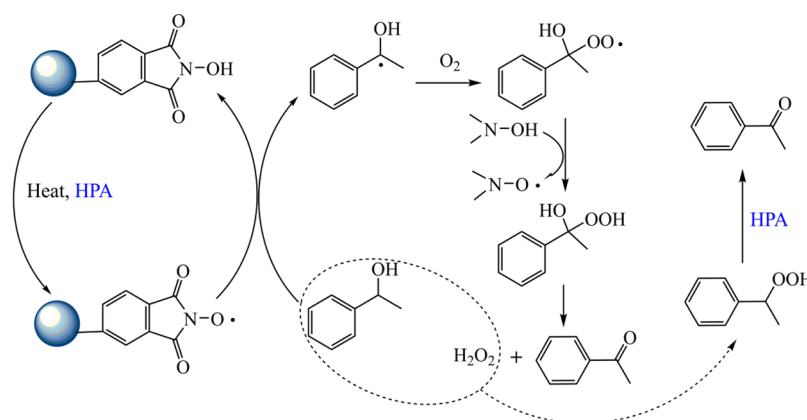
the oxidation was operated in acetonitrile at 80 °C, with only 22% conversion of PEA. A higher PEA conversion of 30% with an AcPO selectivity of 91% was accomplished in acetic acid at 80 °C, which was increased to 42% when the reaction temperature increased to 90 °C (entries 4 and 5; Table 3). At 90 °C, oxidation results were similar in benzonitrile and benzonitrile, which were identifiably inferior to those in acetic acid (entries 2, 3, and 5; Table 3). The comparatively superior catalytic efficiency in acetic acid may be attributed to the fact that the protonation of residual amine groups on HPA enhanced the cocatalysis effect of quaternary ammonium

salts.<sup>50</sup> The conversion and selectivity were decreased to 37 and 87% with a shorter oxidation time of 15 h, respectively (entry 7; Table 3). With extending the oxidation time from 20 to 40 h or increasing the temperature from 90 to 100 °C, there was no obvious change in the catalytic performance of NHPI-HCMSs (entries 5, 6, and 8; Table 3). Moreover, the detected conversion of PEA was significantly increased from 5 to 42% with an oxidation time from 3 to 20 h and kept constant after 20 h (Figure S4). Hence, acetic acid, 90 °C, and 20 h were a suitable reaction solvent, temperature, and time with the addition of an 8 mol % catalyst in our system, respectively.

It was widely recognized that the phthalimide *N*-oxyl (PINO) radical was formed and initiated the free radical chain reaction in the NHPI-catalytic oxidation system.<sup>51</sup> Based on previous literatures,<sup>7,11,12,18</sup> a possible reaction path for the oxidation of PEA with O<sub>2</sub> using NHPI-HCMSs was proposed, as shown in Scheme 3. With the aid of heat and supported HPA, NHPI-HCMSs are transformed into active species (PINO-HCMSs), which abstract a hydrogen atom from PEA to generate related aromatic radicals. The aromatic radical reacts with O<sub>2</sub> and further undergoes H-abstraction from supported NHPI to produce hydroxyl hydroperoxide, which thermally decomposed into hydrogen peroxide and AcPO. Then, H<sub>2</sub>O<sub>2</sub> could oxidize substrate PEA into PEHP. Finally, HPA facilitated the decomposition of PEHP into AcPO.

The reusability and stability of the heterogeneous catalyst were pivotal for its practical application. To test the impact of the recycling process on the oxidation, NHPI-HCMSs were repeatedly utilized as the catalyst six times under the same oxidation conditions (Figure S5). After six runs, NHPI-HCMS still had good catalytic activity with a PEA conversion of 40% and an AcPO selectivity of 93%. The surface property of recycled NHPI-HCMSs was characterized by FTIR and SEM (Figure 4). It was clear that the morphology and surface groups of NHPI-HCMSs were almost unchanged after recycled catalytic oxidation. Based on the excellent catalytic stability and reusability of NHPI-HCMSs, their universality was further evaluated via the catalytic oxidation of various aromatic alcohols and cyclohexanol. All substrates could be smoothly oxidized into relative carbonyl compounds with high selectivity (>85%) and good conversion (Table 4). These facts definitely demonstrated the potential of NHPI-HCMSs in the industrial oxidation.

Table S2 displays the advantage of this heterogeneous catalysis in comparison with those previously reported

**Scheme 3. Plausible Catalytic Oxidation Mechanism of PEA with NHPI-HCMSs**

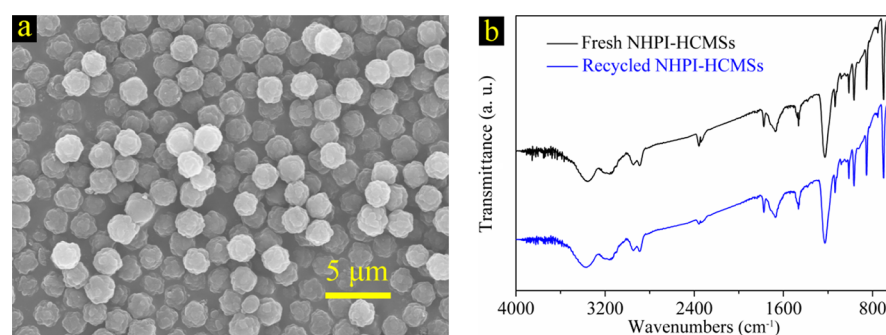


Figure 4. SEM (a) image and FTIR spectrum (b) of recycled NHPI-HCMSs.

Table 4. Catalytic Oxidation of Various Alcohols<sup>a</sup>

Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1			37	86
2			39	98
3			40	92
4			28	94
5			30	93
6			26	92
7 <sup>b</sup>			29	96

<sup>a</sup>The reactions were conducted with a substrate (10 mmol) and supported NHPI (8 mol %) under O<sub>2</sub> (15 mL min<sup>-1</sup>) at 90 °C in CH<sub>3</sub>COOH (25 mL). <sup>b</sup>The oxidation time was prolonged to 40 h.

methods in terms of the catalyst, oxidant, and reaction conditions employed in the selective oxidation of PEA as typical substrates. In brief, designed catalytic oxidation is environmentally beneficial due to the metal-free system utilizing oxygen as a sole oxidant and reusable active catalyst.

### 3. CONCLUSIONS

Monodisperse HCMSSs with hierarchical porosity and NHPI functionalization were fabricated and showed a good catalytic effect on the oxygen oxidation of alcohols as a recyclable and green catalyst. The plentiful mesoporous and macroporous structures were introduced onto HCMSSs via NaOH-impregnated calcination in a static air atmosphere without visible damage of their morphology. The porous HCMSSs were covalently modified with NHPI through multiple quaternization and amidation reactions under mild conditions, which can catalytically convert PEA into AcPO using molecular oxygen as an oxidant. This supported NHPI catalytic system presented superior conversion of PEA and selectivity of AcPO compared to NHPI and displayed a wide applicability in the selective oxidation of various alcohols into carbonyl compounds. The NHPI-HCMSs could be used repeatedly for at least six

reaction cycles without evident reduction of reactivity or change of the surface property. The alluring features of the developed catalytic system are the utilization of molecular oxygen as a green oxidant, green synthesis, and good reusability and stability of the heterogeneous catalyst, which render it verifiable to use in industrial usage.

### 4. EXPERIMENTAL SECTION

**4.1. Chemicals and Materials.** All organic chemicals were obtained from Aladdin Chemical Co., Ltd. (Shanghai, China) and used without further treatment. Hydrochloride (37% in H<sub>2</sub>O) and sodium hydroxide (99.9%) were supplied by Sinopharm Chemical Reagent Co., Ltd. 4-Carboxy-NHPI was synthesized according to the reported classic method and identified by electrospray ionization mass spectrometry.<sup>52</sup> Monodisperse colloidal HCMSSs (2.2 μm) were fabricated via the HTC of sucrose based on a previous work.<sup>53</sup>

**4.2. Production of Hierarchically Porous HCMSSs.** Typically, colloidal HCMSSs (5 g) were dispersed in 5% NaOH solution (35 mL) and soaked for 1 h at 60 °C under magnetic stirring. Then, colloidal HCMSSs were filtered and washed with water until the filtrate was clear and neutral with a pH of 7. After that, impregnated HCMSSs were dried and heated in a crucible with a cover under a static air atmosphere to introduce porosity onto their surface. The heating temperature increased to 850 °C at 5 °C min<sup>-1</sup> and was held for 2 h and then descended to room temperature naturally.

For comparison, conventional KOH-added activation and direct calcination without NaOH impregnation were also conducted with the same temperature programming. In KOH-added activation, the mix of above HCMSSs and KOH solution was dewatered through rotary evaporation after the soak and then underwent carbonization.

#### 4.3. Covalent Functionalization of HCMSSs with NHPI.

Above activated HCMSSs were immersed in hydrochloride solution (10 wt %) and heated to reflux for 3 h, then filtered, and washed with water until the pH of the filtrate was neutral. The solution (20 mL) of 0.4 g of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) and *N*-hydroxysuccinimide (NHS; 0.2 g) was mixed with HCMSSs for 2 h. Then, polyethylene imine (15 wt % in H<sub>2</sub>O, 30 mL) was added and stirred under a nitrogen atmosphere overnight. The subsequent HPA grafting was inspired by reported polymeric quaternization.<sup>54</sup> Briefly, aminated HCMSSs were reacted with 40 mL of ethylene glycol diglycidyl ether (EGDE; 3.5 vol % in water) at 70 °C for 1.5 h and washed with water and ethanol, which were further mixed with 40 mL of methylamine (MA, 3 vol %) under the same conditions; the

above two procedures were repeated twice to construct three layers of HPA. 4-Carboxyl-NHPI was activated by the dichloromethane solution (30 mL) of EDCI (0.4 g) and NHS (0.2 g) for 1 h and reacted with above HPA-modified HCMSs at 45 °C for 10 h. After washing with water and ethanol, NHPI-HCMSs were obtained and dried in an oven (80 °C).

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00176>.

Further information about experimental operation, scheme of the PEA oxidation, FTIR spectra of colloidal HCMSs before and after NaOH impregnation, C1s XPS of activated HCMSs, SEM mapping of nitrogen on NHPI-HCMSs, elemental analysis of HCMSs before and after functionalizations, detected conversion of PEA with reaction time, the recycling of NHPI-HCMSs for the oxidation of PEA into AcPO, and catalytic performances for various heterogeneous catalytic systems in the oxidation of PEA into AcPO (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Chandra, P.; Ghosh, T.; Choudhary, N.; Mohammad, A.; Mobin, S. M. Recent advancement in oxidation or acceptorless dehydrogen-

ation of alcohols to valorised products using manganese based catalysts. *Coord. Chem. Rev.* **2020**, *411*, 213241.

(2) Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. Solvent-free oxidation of primary alcohols to aldehydes using Au-Pd/TiO<sub>2</sub> catalysts. *Science* **2006**, *311*, 362–365.

(3) Alamgholiloo, H.; Rostamnia, S.; Zhang, K.; Lee, T. H.; Lee, Y.-S.; Varma, R. S.; Jang, H. W.; Shokouhimehr, M. Boosting Aerobic Oxidation of Alcohols via Synergistic Effect between TEMPO and a Composite Fe<sub>3</sub>O<sub>4</sub>/Cu-BDC/GO Nanocatalyst. *ACS Omega* **2020**, *5*, 5182–5191.

(4) Behrouzi, L.; Bagheri, R.; Mohammadi, M.-R.; Song, Z.; Chernev, P.; Dau, H.; Najafpour, M.-M.; Kaboudin, B. Electrochemical alcohols oxidation mediated by N-hydroxyphthalimide on nickel foam surface. *Sci. Rep.* **2020**, 19378.

(5) Zhou, L.; Wu, H.; Yang, X.; Su, Y.; Chen, C.; Xu, J. Selective oxidation of cellulose catalyzed by NHPI/Co(OAc)<sub>2</sub> using air as oxidant. *Cellulose* **2014**, *21*, 4059–4065.

(6) Melone, L.; Punta, C. Metal-free aerobic oxidations mediated by N-hydroxyphthalimide. A concise review. *Beilstein J. Org. Chem.* **2013**, *9*, 1296–1310.

(7) Zhou, L.-P.; Zhang, C.-F.; Fang, T.; Zhang, B.-B.; Wang, Y.; Yang, X.-M.; Zhang, W.; Xu, J. Selective oxidation of alcohols catalyzed by a transition metal-free system of NHPI/DDQ/NaNO<sub>2</sub>. *Chin. J. Catal.* **2011**, *32*, 118–122.

(8) Tavallaei, H.; Jafarpour, M.; Feizpour, F.; Rezaeifard, A.; Farrokhi, A. A cooperative effect in a novel bimetallic Mo-V nanocomplex catalyzed selective aerobic C-H Oxidation. *ACS Omega* **2019**, *4*, 3601–3610.

(9) Nakamura, R.; Obora, Y.; Ishii, Y. Synthesis of 6-hydroxy-2-naphthoic acid from 2,6-diisopropyl-naphthalene using NHPI as a key catalyst. *Tetrahedron* **2009**, *65*, 3577–3581.

(10) Guha, S. K.; Obora, Y.; Ishihara, D.; Matsubara, H.; Ryu, I.; Ishii, Y. Aerobic oxidation of cyclohexane using N-hydroxyphthalimide bearing fluoroalkyl chains. *Adv. Synth. Catal.* **2008**, *350*, 1323–1330.

(11) Hu, Y.; Chen, L.; Li, B. NHPI/tert-butyl nitrite: A highly efficient metal-free catalytic system for aerobic oxidation of alcohols to carbonyl compounds using molecular oxygen as the terminal oxidant. *Catal. Commun.* **2016**, *83*, 82–87.

(12) Zhou, W.; Chen, D.; Cui, A.; Qian, J.; He, M.; Chen, Q. Aerobic oxidation of alcohols to carbonyl compounds catalyzed by N-hydroxyphthalimide (NHPI) combined with CoTPP-Zn<sub>2</sub>Al-LDH. *J. Chem. Sci.* **2017**, *129*, 295–299.

(13) Huang, Z.; Xia, Y.-T.; Wen, L.-Y.; Gao, L.; Luo, Y.-B. Research progress in N-hydroxyphthalimide-based heterogeneous catalysts. *Modern Chem. Ind.* **2018**, *38*, 16–20.

(14) Coseri, S. A new and efficient heterogeneous system for the phthalimide N-oxyl (PINO) radical generation. *Eur. J. Org. Chem.* **2007**, *2007*, 1725–1729.

(15) Zhou, M.; Li, X.; Bao, L.; Yuan, X.; Luo, H. A new method for immobilization of NDHPI on SBA-15 carrier used as catalyst for selective oxidation of toluene. *Catal. Lett.* **2016**, *146*, 383–390.

(16) Dobras, G.; Kasperczyk, K.; Jurczyk, S.; Orlińska, B. N-hydroxyphthalimide supported on silica coated with ionic liquids containing CoCl<sub>2</sub> (SCILLs) as new catalytic system for solvent-free ethylbenzene oxidation. *Catalysts* **2020**, DOI: 10.3390/catal10020252..

(17) Rajabi, F.; Luque, R.; Clark, J.-H.; Karimi, B.; Macquarrie, D.-J. A silica supported cobalt (II) Salen complex as efficient and reusable catalyst for the selective aerobic oxidation of ethyl benzene derivatives. *Catal. Commun.* **2011**, *12*, 510–513.

(18) Gao, B.; Bi, C. Some catalytic characteristics of compositional catalysts of immobilized N-hydroxyphthalimide and metal salts in aerobic oxidation of 1-phenylethanol. *Catal. Commun.* **2018**, *115*, 6–11.

(19) Culica, M.-E.; Kasperczyk, K.; Baron, R.-I.; Biliuta, G.; Macsim, A.-M.; Lazea-Stoyanova, A.; Orlińska, B.; Coseri, S. Recyclable



polymer-supported *N*-hydroxyphthalimide catalysts for selective oxidation of pullulan. *Materials* **2019**, *12*, 3585–3596.

(20) Petroselli, M.; Franchi, P.; Lucarini, M.; Punta, C.; Melone, L. Aerobic oxidation of alkylaromatics using a lipophilic *N*-hydroxyphthalimide: overcoming the industrial limit of catalyst solubility. *ChemSusChem* **2014**, *7*, 2695–2703.

(21) Blandez, J. F.; Navalón, S.; Álvaro, M.; García, H. *N*-hydroxyphthalimide anchored on diamond nanoparticles as a selective heterogeneous metal-free oxidation catalyst of benzylic hydrocarbons and cyclic alkenes by molecular O<sub>2</sub>. *ChemCatChem* **2018**, *10*, 198–205.

(22) Titirici, M. M.; Antonietti, M. Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. *Chem. Soc. Rev.* **2010**, *39*, 103–116.

(23) Lian, L.; Jiang, X.; Lv, J.; Bai, F.; Zhu, B.; Lou, D. Fabrication of glucose-derived carbon-decorated magnetic microspheres for extraction of bisphenols from water and tea drinks. *J. Sep. Sci.* **2019**, *42*, 3451–3458.

(24) Zhao, Q.; Wu, S.; Zhang, P.; Zhu, Y. Hydrothermal carbonaceous sphere based stationary phase for anion exchange chromatography. *Talanta* **2017**, *163*, 24–30.

(25) Shao, J.; Qu, Q.; Wan, Z.; Gao, T.; Zuo, Z.; Zheng, H. From dispersed microspheres to interconnected nanospheres: carbon-sandwiched mono layered MoS<sub>2</sub> as high-performance anode of Li-ion batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 22927–22934.

(26) Liu, J.; Wickramaratne, N. P.; Qiao, S. Z.; Jaroniec, M. Molecular-based design and emerging applications of nanoporous carbon spheres. *Nat. Mater.* **2015**, *14*, 763–774.

(27) Doke, D. S.; Umbarkar, S. B.; Gawande, M. B.; Zboril, R.; Biradar, A. V. Environmentally benign bioderived carbon microspheres-supported molybdena nanoparticles as catalyst for the epoxidation reaction. *ACS Sustainable Chem. Eng.* **2016**, *5*, 904–910.

(28) Renz, M. *Hydrothermal Carbonization and Its Role in Catalysis*; John Wiley & Sons, Ltd: 2017.

(29) Demir-Cakan, R.; Makowski, P.; Antonietti, M.; Goettmann, F.; Titirici, M. M. Hydrothermal synthesis of imidazole functionalized carbon spheres and their application in catalysis. *Catal. Today* **2010**, *150*, 115–118.

(30) Ibrahim, S. F.; Asikin-Mijan, N.; Ibrahim, M. L.; Abdulkareem-Alsultan, G.; Izham, S.-M.; Taufiq-Yap, Y.-H. Sulfonated functionalization of carbon derived corncob residue via hydrothermal synthesis route for esterification of palm fatty acid distillate. *Energy Convers. Manage.* **2020**, 112698.

(31) Wataniyakul, P.; Boonnoun, P.; Quitain, A. T.; Sasaki, M.; Kida, T.; Laosiripojana, N.; Shotipruk, A. Preparation of hydrothermal carbon as catalyst support for conversion of biomass to 5-hydroxymethylfurfural. *Catal. Commun.* **2018**, *104*, 41–47.

(32) Laohapornchaiphon, J.; Smith, C. B.; Smith, S. M. One-step preparation of carbon-based solid acid catalyst from water hyacinth leaves for esterification of oleic acid and dehydration of xylose. *Chem.-Asian J.* **2017**, *12*, 3178–3186.

(33) Advani, J. H.; Singh, A. S.; Khan, N.-U. H.; Bajaj, H. C.; Biradar, A. V. Black yet green: Sulfonic acid functionalized carbon as an efficient catalyst for highly selective isomerization of  $\alpha$ -pinene oxide to trans-carveol. *Appl. Catal., B* **2020**, 118456.

(34) Fang, W.; Fan, Z.; Shi, H.; Wang, S.; Shen, W.; Xu, H.; Clacens, J.-M.; De Campo, F.; Liebens, A.; Pera-Titus, M. Aquivion®-carbon composites via hydrothermal carbonization: amphiphilic catalysts for solvent-free biphasic acetalization. *J. Mater. Chem. A* **2016**, *4*, 4380–4385.

(35) Zhang, Z.; Liu, C.; Liu, D.; Shang, Y.; Yin, X.; Zhang, P.; Mamba, B.-B.; Kuvarega, A.-T.; Gui, J. Hydrothermal carbon-supported Ni catalysts for selective hydrogenation of 5-hydroxymethylfurfural toward tunable products. *J. Mater. Sci.* **2020**, *55*, 14179–14196.

(36) Xie, L.; Li, X.; Deng, J.; Gong, Y.; Wang, H.; Mao, S.; Wang, Y. Sustainable and scalable synthesis of monodisperse carbon nanospheres and their derived superstructures. *Green Chem.* **2018**, *20*, 4596–4601.

(37) Guo, L.; Zhang, P.; Cui, Y.; Liu, G.; Wu, J.; Yang, G.; Yoneyama, Y.; Tsubaki, N. One-pot hydrothermal synthesis of nitrogen functionalized carbonaceous material catalysts with embedded iron nanoparticles for CO<sub>2</sub> hydrogenation. *ACS Sustainable Chem. Eng.* **2019**, *7*, 8331–8339.

(38) Yuan, M.; Long, Y.; Yang, J.; Hu, X.; Xu, D.; Zhu, Y.; Dong, Z. Biomass Sucrose-derived cobalt@nitrogen-doped carbon for catalytic transfer hydrogenation of nitroarenes with formic acid. *ChemSusChem* **2018**, *11*, 4156–4165.

(39) Romero-Anaya, A. J.; Ouzzine, M.; Lillo-Ródenas, M. A.; Linares-Solano, A. Spherical carbons: Synthesis, characterization and activation processes. *Carbon* **2014**, *68*, 296–307.

(40) Xu, M.; Yu, Q.; Liu, Z.; Lv, J.; Lian, S.; Hu, B.; Mai, L.; Zhou, L. Tailoring porous carbon spheres for supercapacitors. *Nanoscale* **2018**, *10*, 21604–21616.

(41) Roberts, A. D.; Li, X.; Zhang, H. Porous carbon spheres and monoliths: morphology control, pore size tuning and their applications as Li-ion battery anode materials. *Chem. Soc. Rev.* **2014**, *43*, 4341–4356.

(42) Matsunaka, K.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. A remarkable effect of quaternary ammonium bromide for the *N*-hydroxyphthalimide-catalyzed aerobic oxidation of hydrocarbons. *Tetrahedron Lett.* **1999**, *40*, 2165–2168.

(43) Mao, L.; Zhang, Y.; Hu, Y.; Ho, K. H.; Ke, Q.; Liu, H.; Hu, Z.; Zhao, D.; Wang, J. Activation of sucrose-derived carbon spheres for high-performance supercapacitor electrodes. *RSC Adv.* **2015**, *5*, 9307–9313.

(44) Chen, Z.; Ma, L.; Li, S.; Geng, J.; Song, Q.; Liu, J.; Wang, C.; Wang, H.; Li, J.; Qin, Z.; Li, S. Simple approach to carboxyl-rich materials through low-temperature heat treatment of hydrothermal carbon in air. *Appl. Surf. Sci.* **2011**, *257*, 8686–8691.

(45) Contescu, A.; Contescu, C.; Putyera, K.; Schwarz, J. A. Surface acidity of carbons characterized by their continuous pK distribution and Boehm titration. *Carbon* **1997**, *35*, 83–94.

(46) Du, Z.; Sun, Z.; Zhang, W.; Miao, H.; Ma, H.; Xu, J. A free radical process for oxidation of hydrocarbons promoted by nonmetal xanthone and tetramethylammonium chloride under mild conditions. *Tetrahedron Lett.* **2009**, *50*, 1677–1680.

(47) Zhang, P.; Wang, C.; Chen, Z.; Li, H. Acetylacetone-metal catalyst modified by pyridinium salt group applied to the NHPI-catalyzed oxidation of cholesteryl acetate. *Catal. Sci. Technol.* **2011**, *1*, 1133–1137.

(48) Xu, Y.; Zhen, G.; Tian, Z.; Zhao, J. The catalytic oxidation activities of NHPI and quaternary ammonium. *J. Jinan Univ.* **2014**, *28*, 01.

(49) Deng, W.; Wan, Y.-p.; Jiang, H.; Luo, W.-P.; Tan, Z.; Jiang, Q.; Guo, C.-C. Solvent-free aerobic oxidation of toluene over metalloporphyrin/NHPI/CTAB: synergy and mechanism. *Catal. Lett.* **2014**, *144*, 333–339.

(50) Zhao, Q.; Chen, K.; Zhang, W.; Yao, J.; Li, H. Efficient metal-free oxidation of ethylbenzene with molecular oxygen utilizing the synergistic combination of NHPI analogues. *J. Mol. Catal. A: Chem.* **2015**, *402*, 79–82.

(51) Coseri, S. Phthalimide-*N*-oxyl (PINO) radical, a powerful catalytic agent: its generation and versatility towards various organic substrates. *Catal. Rev.* **2009**, *51*, 218–292.

(52) Sawatari, N.; Yokota, T.; Sakaguchi, S.; Ishii, Y. Alkane Oxidation with Air Catalyzed by Lipophilic *N*-Hydroxyphthalimides without Any Solvent. *J. Org. Chem.* **2001**, *66*, 7889–7891.

(53) Gong, Y.; Xie, L.; Li, H.; Wang, Y. Sustainable and scalable production of monodisperse and highly uniform colloidal carbonaceous spheres using sodium polyacrylate as the dispersant. *Chem. Commun.* **2014**, *50*, 12633–12636.

(54) Pohl, C.; Saini, C. New developments in the preparation of anion exchange media based on hyperbranched condensation polymers. *J. Chromatogr. A* **2008**, *1213*, 37–44.