Synthesis of Sustainable and Robust Heterogeneous TEMPO Catalyst utilizing Activated Carbon for Aerobic Alcohol Oxidation

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Abstract

The selective oxidation of alcohols is a crucial process in organic chemistry, but current methodologies have limitations such as pollution and over-oxidation. The use of 2,2,6,6-tetramethylpiperidine oxide (TEMPO) as a catalyst offers a promising approach for selective aerobic alcohol oxidation. However, the high cost of TEMPO and difficulty in catalyst recycling hinder its industrial application. This study focuses on developing a sustainable and robust heterogeneous TEMPO catalyst by immobilizing TEMPO on activated carbon (AC) through ozonation and reductive amination. The surface modification of AC through ozone carbonylation is explored, and a green and safe process is established using water as a dispersing and heat-shifting medium. The TEMPO-functionalized AC as a heterogeneous catalyst is characterized using various analytical techniques, and its catalytic performance is evaluated for continuous aerobic alcohol oxidation in a micro-packed bed reactor. The results demonstrate an extended catalyst lifetime (turnover number reaches 1465.0 for benzyl alcohol oxidation) and significant potential for industrial applications.

Keywords: TEMPO, heterogeneous catalysis, aerobic alcohol oxidation, surface modification, activated carbon

1. Introduction

The selective oxidation of alcohols (**Fig. 1**) is one of significant branches within the field of organic chemistry,¹ which plays a crucial role in both modern industry and synthetic chemistry.², ³ However, prior methodologies, such as manganese and chromium as oxidants,^{4, 5} as well as high-valent iodine compounds,⁶ suffer from the limitations of severe pollution and a tendency to promote over-oxidation, leading to the undesired formation of carboxylic acids. On the contrary, the utilization of 2,2,6,6-tetramethylpiperidine oxide (TEMPO) as a catalyst, in conjunction with tert-butyl nitrite (TBN), offers a highly promising approach to achieve the selective oxidation of alcohols with oxygen as the oxidant.^{7, 8} This catalytic system, known as the TEMPO/TBN/O₂ system, exhibits notable advantages including high efficiency, excellent selectivity, and environmental friendliness (with water being the sole by-product).⁹ These attributes make it an appealing option to carry on selective oxidations of alcohols for production.



Fig. 1 Selective oxidation of alcohols.

Nevertheless, a noteworthy obstacle to its industrial application remains, namely the high cost of TEMPO and the challenge of catalyst recycling within homogeneous reactions.^{7, 10} Accordingly, there is growing interest in the immobilization of TEMPO on solid supports to develop heterogeneous catalysts to enable recyclability. Previous studies have successfully immobilized certain TEMPO derivatives (such as 4-hydroxy-TEMPO and 4-amino-TEMPO) onto various types of supports, including silica,¹¹⁻¹³ carbon materials,^{14, 15} polymers,^{16, 17} metal-organic frameworks (MOF),¹⁸ and covalent-organic frameworks (COF).¹⁹ Among these methods, covalent grafting has been extensively investigated due to the chemical bond rigidity.²⁰

To prolong the duration of TEMPO grafted catalysts, the surface properties of the supports should be considered as a primary factor. Silica-supported TEMPO catalysts have shown compromised stability, for the maximum turnover number (TON) is about 239 (achieved by Machado et. al using TEMPO grafted MCM-41²¹) for the conversion of benzyl alcohol to benzaldehyde (template reaction in this study, referred to as such hereinafter), likely due to the weakness of the surface Si-O bond. Conversely, carbon materials, with robust surface chemistry, have significantly enhanced heterogeneous TEMPO catalyst lifetimes. Among them, our group successfully grafted TEMPO onto the surface of activated carbon (AC), achieving a TON of 326.9 for the template reaction.²²

In addition to supports, the grafting strategy also plays an essential role in determining the stability of heterogeneous TEMPO catalysts. Catalysts with stronger covalent bonds exhibit longer lifetimes. Commonly used grafting strategies involve ether, ester, amide, and amine bonds linkage. However, the former three types of bonds are susceptible to hydrolysis in acidic conditions, resulting in grafted catalysts with relatively low stability. In contrast, amine bonds exhibit greater durability under moderately acidic or basic conditions, thus enabling extended catalyst lifetimes, by which Karimi et al. successfully grafted TEMPO moieties onto the surface of aminopropyl-functionalized magnetic nanoparticles, achieving a pronounced TON (turnover number) increase to 500.²³

Based on the previous findings, the combination of AC as a support and the grafting of amine bonds holds significant promise in enhancing the robustness of heterogeneous TEMPO catalysts. However, a notable challenge arises from the limited presence of surface functional groups (such as carbonyl or amino groups) on AC,²⁴ which are essential for the amination reaction between AC and TEMPO to form a linkage. Currently, widely employed methods for surface modification of AC include direct oxidation using hydrogen peroxide,²⁵ nitric acid,²⁶ and ozone.²⁷ However, these methods are relatively harsh and tend to increase the carboxyl groups instead of carbonyl groups. Conversely, there is a dearth of methods on surface-carbonylation of AC. In this regard, our previous work successfully demonstrated the efficient formylation on AC using a Grignard reagent.²⁸ Nevertheless, the process still faces challenges related to convenience, economic viability, and environmental sustainability.

In this study, we propose an innovative approach that utilizes water as a dispersing and heatshifting medium to regulate the interaction between AC and ozone. This enables the development of a green, mild, and safe process specifically designed for carbonylation modification. Subsequently, a reductive amination strategy was employed to immobilize TEMPO on the ozonecarbonylated AC for the first time. To verify the successful ozone carbonylation and TEMPO grafting, elemental analysis (EA), acid-base titration, X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), thermogravimetric analysis (TGA), electron paramagnetic resonance (EPR), and scanning electron microscopy (SEM) were performed. Finally, the catalytic performance was evaluated in a micro-packed bed reactor (µPBR) using the template reaction, demonstrating a considerable extension of the lifetime of the heterogeneous TEMPO catalyst.

2. Materials and methods

2.1 Chemicals

Activated carbons (size: 250-300 μm) were purchased from Sigma-Aldrich Inc. Benzyl alcohol (99.9%) and acetonitrile (99.9%) were supplied by Beijing Lanyi Chemical Products, Co., Ltd. 4-amino-2,2,6,6-tetramethyl piperidine-noxyl was purchased from Myrell Chemical Technology Co., Ltd. Sodium cyanoborohydride was bought from Bide Pharmatech Co., Ltd.

Sodium sulfite was purchased from Beijing Tongguang Fine Chemical Co., LTD. Oxygen (99.9%) was supplied by Air Liquide in China Co., Ltd.

2.2 Equipment and mode for ozonation of AC

To explore the optimal conditions for carbonylation of AC surfaces in this study, condition screening of ozone treatment was conducted with two distinct modes: in a Bubbly Batch Reactor (**B** mode) and in a μ PBR (**P** mode).

As illustrated in **Fig. 2**, oxygen from a gas source was passed through an ozone generator to generate approximately 100 mg/L of ozone, and its pressure and flow rate were controlled by a pressure-reducing valve and a mass flow meter, respectively.

For **B** mode, as shown in **Fig. 2(a)**, the AC particles were stirred in a batch reactor together with ultrapure water, while ozone was introduced into the reaction system through a bubble diffuser. After a certain duration of bubbling reaction, a fixed amount of saturated sodium sulfite solution was added to quench the reaction. Finally, the ozone-treated AC was obtained through filtration, water washing, and drying. After the screening experiments (see **Supplementary Information**), the sample with the best carbonylation results was selected for TEMPO immobilization and was denoted as **B-ozo-AC**.

For **P** mode in **Fig. 2(b)**, ozone and ultrapure water were pre-mixed in a T-junction mixer and directly fed into a μ PBR packed with AC particles. To mitigate the potential exothermic effect resulting from significantly reduced mass transfer resistance in this reactor, the temperature was maintained at 0°C using an ice bath. After a certain duration of ozone treatment, and a flow of saturated sodium sulfite solution would replace ultrapure water to quench the reaction. Eventually, the AC particles were treated by water washing and air drying to attain the ozonized AC. After the

screening experiments (see **Supplementary Information**), the optimal carbonylated sample was chosen as supports for TEMPO grafting and was denoted as **B-ozo-AC**.



Fig. 2 Platform for carrying on ozonation of AC: (a) B mode; (b) P mode.

2.3 TEMPO immobilization on ozonized AC



Fig. 3 Scheme on preparation of TEMPO-functionalized AC in this study.

To immobilize TEMPO on ozone treated AC using the reductive amination strategy, 4-amino-TEMPO in methanol was stirred with **B-ozo-AC** or **P-ozo-AC** in a flask at room temperature for 72 hours. During this period, sodium cyanoborohydride was added to the reaction system at 12 hours, 24 hours, and 48 hours, respectively. Subsequently, the mixture was filtered and dried, yielding AC loaded with TEMPO molecules. This material was designated as **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO**. Fig. 3 depicts an overall procedure on preparation of this heterogeneous TEMPO catalyst.

2.4 Experimental setup for continuous aerobic alcohol oxidation

The aerobic oxidation of alcohols was conducted using another µPBR (length: 16.0 cm, diameter: 4.00 mm) containing the **B-ozo-AC-TEMPO** or **P-ozo-AC-TEMPO** catalyst (mass: 1.2 g, size: 250-300 µm). **Fig. 4** illustrates the equipment employed for continuous aerobic alcohol oxidation. To ensure precise delivery of oxygen and substrate solution, a mass flow controller and a liquid flow metering pump were utilized. The gas and liquid phases were mixed in a T-junction mixer, while the reaction temperature and pressure were maintained using a water bath and a back-pressure regulator, respectively. The samples at the outlet were subsequently analyzed using gas chromatography, with toluene serving as the internal standard.



Fig. 4 Experimental setup for continuous aerobic alcohol oxidation

For the template reaction, the Conversion, Selectivity, and Yield of oxidation from benzyl alcohol to benzaldehyde were calculated by:

$$Conversion = \frac{C_{BnOH,s} - C_{BnOH,p}}{C_{BnOH,s}} \times 100\%$$
(1)

Selectivity =
$$\frac{C_{\text{BzH},p}}{C_{\text{BnOH},s} - C_{\text{BnOH},p}} \times 100\%$$
 (2)

$$\text{Yield} = \frac{C_{\text{BzH},p}}{C_{\text{BnOH},s}} \times 100\% \tag{3}$$

where $C_{BnOH,s}$ is the molar concentration of benzyl alcohol in the substrate solution, $C_{BnOH,p}$, and $C_{BzH,p}$ are the molar concentrations of benzyl alcohol and benzaldehyde in the product, respectively. All these parameters are obtained during continuous aerobic oxidation at a specific reaction time.

The residence time (τ) was defined as:

$$\tau = \frac{\pi d^2 L \cdot h \cdot \varepsilon}{4F} \tag{4}$$

where d and L represent the inner diameter and the length of the μ PBR, respectively. h is the liquid holdup, ε is the bed porosity, F is the liquid flow rate.

The TEMPO loading (mmol/g) on B(P)-ozo-AC-TEMPO (M_{TEMPO}) was derived from:

$$M_{\text{TEMPO}} = \frac{N_{B(P)-ozo-AC-TEMPO} - N_{B(P)-ozo-AC}}{2M_N}$$
(5)

where N_X is the nitrogen mass content of the sample *X*, obtained by elemental analysis, M_N is the molar mass of the nitrogen atom.

The TON and TOF values of this catalyst were defined as:

$$TON = \frac{n_p}{n_{cat}}$$
(6)

$$TOF = \frac{n_p}{n_{cat}t} \tag{7}$$

where n_p is the converted mole number of substrates, n_{cat} is the mole number of TEMPO immobilized on the catalyst, and t is the total reaction time.

3. Results and discussion

3.1 Characterization of AC and catalysts



Fig. 5 Characterization results: (a) IR; (b) TGA; (c) C 1s XPS; (d) N 1s XPS; (e) EPR; (f) EA and TA.

Above all, IR was utilized to gain a comprehensive understanding of the surface properties of the five samples (AC, **B-ozo-AC**, **P-ozo-AC**, **B-ozo-AC-TEMPO**, and **P-ozo-AC-TEMPO**). As depicted in **Fig. 5(a)**, the absorption peaks at 3440 cm⁻¹ and 1631 cm⁻¹ can be attributed to the stretching vibrations of O-H and C=C, respectively.²⁹ These peaks indicate the presence of abundant oxygen-containing groups and C=C bonds on AC. However, the slight variation observed among the five samples is insufficient to serve as an indicator for ozonation and TEMPO immobilization.

Subsequently, TGA was performed on **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO** to confirm the successful immobilization of TEMPO. As shown in **Fig. 5(b)**, both samples exhibit significant mass loss in the temperature range of 150 to 450°C, which aligns with the decomposition temperature reported in literature,^{22, 30} suggesting efficacious immobilization of TEMPO moieties onto AC. Furthermore, the TGA curves allow for a rough estimation of the

TEMPO loading, approximately 0.3 and 0.9 mmol/g for **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO**, respectively. This result implies that **P** mode may be more suitable for surface-carbonylation and TEMPO immobilization.

To provide a comprehensive and quantitative characterization of the effects induced by ozonation and TEMPO immobilization on AC, XPS analysis was conducted on the same five samples. The C 1s spectra are presented in **Fig. 5(c)**. The peaks observed at 284.6, 285.3, 286.5, 288.3, 290.1, and 291.2 eV can be assigned to carbon atoms in C=C, C-C or C-N, C-O, C=O, O-C=O, and carbonates, respectively.³¹ It is worth noting that the intensity of the C=O peak is higher in **B-ozo-AC** and **P-ozo-AC** compared to AC, indicating an enhanced carbonylation following ozone treatment, with **P** mode exhibiting a greater carbonylation capacity than **B** mode. Upon TEMPO immobilization, the intensity of the C=O peak decreases for both **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO**, suggesting that the C=O groups are consumed during the reductive amination for covalent TEMPO grafting.

The N 1s spectra shown in **Fig. 5(d)** consist of peaks at 399.0, 401.2, and 405.4 eV, corresponding to amino-N, pyridinic-N, and nitro-N, respectively.³² Enhanced intensities of the N peaks are observed in **B-ozo-AC** and **P-ozo-AC**, in comparison to crude AC, which indicates that the ozone treatment leads to the depletion of carbon atoms through oxidation, resulting in a relatively higher enrichment of nitrogen atoms. Following the reductive amination with 4-amino-TEMPO, these N peaks become even more prominent, particularly for the amino-N peaks, providing additional evidence for the successful immobilization of TEMPO. Notably, a new peak at 400.1 eV appears in the spectra of **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO**, implying effective TEMPO grafting with well-preserved nitroxyl groups.³³ This finding is consistent with

the TEMPO loadings calculated by TGA, as **P-ozo-AC-TEMPO** displays a stronger intensity in the nitroxyl peak compared to **B-ozo-AC-TEMPO**.

To provide explicit evidence for the effective TEMPO immobilization on AC, EPR analysis was conducted on AC, **B-ozo-AC-TEMPO**, and **P-ozo-AC-TEMPO**. As depicted in **Fig. 5(e)**, with a premise that the correlation between the EPR peak intensity and nitroxyl group content is proportional,³⁴ it could directly confirm the successful TEMPO immobilization on AC, along with the presence of intact nitroxyl groups, because both **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO** exhibit clear EPR peaks, while AC does not. Moreover, the significantly higher peak intensity in **P-ozo-AC-TEMPO** implies a higher loading of TEMPO on this material.

Further quantitative characterizations are necessary to elucidate the alterations in surface functional groups induced by ozonation. To address this, titration was employed to investigate the surface carboxyl groups on AC, **B-ozo-AC**, and **P-ozo-AC**.³⁵ The original AC was titrated to exhibit approximately 0.2 mmol/g of carboxyl groups on its surface. However, as illustrated in **Fig. 5**(**f**), the carboxyl group content decreases to nearly zero after ozonation, presumably due to the decarboxylase reaction facilitated by ozone treatment. Although both EA and titration are unable to detect carbonyl groups, it is reasonable to hypothesize that 4-amino-TEMPO can be immobilized through two primary pathways during the grafting step: amidation with carboxyl groups and reductive amination with carbonyl groups. Therefore, by obtaining more accurate values for the maximum TEMPO loading through EA, it is possible to estimate the approximate carbonyl group content, the TEMPO loadings were determined to be 0.347 and 0.902 mmol/g for **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO**, respectively. These values align with the previous characterizations and further validate the effective covalent grafting through reductive amination.



Fig. 6 SEM images of (a) B-ozo-AC; (b) B-ozo-AC-TEMPO; (c) P-ozo-AC; (d) P-ozo-AC-

TEMPO.



Fig. 7 Elemental distributions by SEM-EDS: (a) B-ozo-AC; (b) B-ozo-AC-TEMPO; (c) P-ozo-AC; (d) P-ozo-AC-TEMPO.

Consequently, the surface morphologies of **B-ozo-AC**, **P-ozo-AC**, **B-ozo-AC-TEMPO**, and **P-ozo-AC-TEMPO** were examined through SEM-EDS. **Fig. 6(a)** displays the distinct porous structure of **B-ozo-AC**, whereas **Fig. 6(b)** reveals that the surface of **B-ozo-AC-TEMPO** becomes

denser following TEMPO grafting. Comparatively, the **P** mode ozone-treated sample in **Fig. 6(b)** appears to possess a less porous structure than **B-ozo-AC**. However, the surface becomes even smoother after TEMPO grafting, suggesting that the pores may be obstructed by TEMPO moieties. Moreover, surface elemental distribution variations are evident from the EDS mapping depicted in **Fig. 7**. Notably, nitrogen demonstrates a uniform distribution across all samples, albeit exhibiting higher density in **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO** compared to **B-ozo-AC** and **P-ozo-AC**, respectively. This observation can be attributed to the presence of grafted TEMPO, which serves as additional evidence for the successful TEMPO immobilization.



Fig. 8 BET analysis results: (a) adsorption-desorption curves; (b) pore size distribution.

To investigate the structural changes induced by ozonation and TEMPO immobilization and establish a foundation for discussing the structure-activity relationship, a quantitative measure using BET analysis was employed. Fig. 8(a) presents the surface area results derived from the adsorption-desorption curves. It is observed that the surface area experiences a slight decrease following **B** mode ozone treatment, while a significant reduction is observed after **P** mode treatment. This reduction can be attributed to the stronger oxidation capacity of the **P** mode, which generates an abundance of oxygen-containing groups that hinder surface accessibility. This

observation aligns with the SEM image findings illustrated in **Fig. 6**. Furthermore, the surface area of **B-oxo-AC-TEMPO** and **P-oxo-AC-TEMPO** is dramatically diminished due to the occupation of TEMPO moieties on the surface.

To determine the pore size distributions, the Barret-Joyner-Halenda method was employed. **Fig. 8(b)** depicts the obtained results, which indicate that ozone treatment leads to a considerable expansion of the AC pores.³⁶ In the case of **B** mode treatment, there is a substantial enhancement in macropores, which is advantageous for TEMPO grafting and heterogeneous catalysis by reducing internal diffusion resistance. Similarly, **P** mode treatment results in a more pronounced increase in mesopores compared to macropores, also indicative of favorable pore expansion. Finally, upon reductive amination with 4-amino-TEMPO, a slight decrease in pore size is observed for **B-oxo-AC-TEMPO** and **P-oxo-AC-TEMPO**, further demonstrating that the TEMPO branches effectively occupy the pores.

3.2 Catalytic performance

3.2.1 Activity and stability

The catalytic activities of the catalysts were evaluated at 5 bar and 80°C with a high feed flow rate (O₂: 50 mL/min, solution: 5 mL/min) to obtain TOF values. With the template reaction performed, the TOFs of **B-ozo-AC-TEMPO** and **P-ozo-AC-TEMPO** were 107.5 and 59.6 h⁻¹, respectively.

Subsequently, long-term catalytic tests were carried out under milder conditions (50°C with a low feed flow rate, **Fig. 9**), maintaining the conversion and selectivity of template reaction at 100% as long as possible. **Fig. 9** shows that both catalysts exhibit a lifetime of approximately 80 hours, with catalyst deactivation assumed when the conversion dropped below 96%. However,

their TONs differ significantly, with B-ozo-AC-TEMPO achieving a TON of 1465.0 and P-ozo-AC-TEMPO achieving only 541.3.



Fig. 9 Long-term catalytic performance of (a) B-ozo-AC-TEMPO (b) P-ozo-AC-TEMPO.

Surprisingly, despite having only about one-third of the TEMPO loading compared to **P-ozo-AC-TEMPO**, **B-ozo-AC-TEMPO** exhibits superior catalytic performance in terms of TON and TOF. This can be attributed to the structure-activity relationship. Apart from TEMPO loading, the pore structure is another differentiating factor between the two catalyst types. The larger surface area and higher proportion of macropores in **B-ozo-AC-TEMPO** effectively utilize the surface-grafted TEMPO moieties for catalysis, reducing internal diffusion resistance and maintaining high activity. Moreover, it is worth noting that **P-ozo-AC-TEMPO**, despite its lower performance, is still valuable due to its ease of continuous preparation through ozone treatment in a µPBR, making it more suitable for potential industrial scale-up. Lastly, the deactivation was still observed in **Fig. 9** after 80 hours, suggesting a potential loss of TEMPO moieties due to C-N bond breakage.

3.2.2 Comparison with other catalysts in literature

 Table 1 presents a comprehensive compilation of reported heterogeneous TEMPO catalysts

 for the template reaction. Previous studies have reported TON (an effective standard for lifetime

assessment) values ranging from 20 to 1160.6. Remarkably, this work has enhanced TON to 1465.0 (Entry 12), owing to the combined stability of AC as support and the covalent graft C-N bond.

Table 1 Comparison of the catalytic performances of covalently grafted TEMPO catalysts in

 literature and this study for the aerobic oxidation of benzyl alcohol.

Entry	Supports	Grafting strategies	TEMPO loading (mmol g ⁻¹)	Oxidant	Yield (%)	TON	TOF (h ⁻¹)	Reference
1	PEG	Etherification	_	O ₂	99	20	6.7	37
2	UiO-67	Etherification	_	Air	>99	99	11	38
3	Silica	"Click" reaction	0.29	O ₂	57	228	57	11
4	Silica	"Click" reaction	0.25	O ₂	>99	20	5.5	39
5	AgNP	Esterification	1.39	O ₂	>99	236.0	94.4	40
6	AC	Esterification	0.6	O ₂	>99	165.5	110.3	22
7	MIL-101	Amidation	_	O ₂	>99	40	13.3	41
8	JUC-566	Amidation	1.25	O ₂	>99	_	132	19
9	AC	Amidation	0.6	O ₂	>99	328.9	135.9	22
10	AMNP	Amination	0.3	O ₂	>99	500.0	125	23
11	AC	Amination	0.410	O ₂	>99	1160.6	99.6	28
12	AC	Amination	0.347	O ₂	>99	1465.0	107.5	This work
13	AC	Amination	0.902	O ₂	>99	541.3	59.6	This work

Furthermore, notable correlation has been observed between catalyst stability and the grafting strategy employed. Generally, in acidic aqueous conditions, amines are assumed to be integral even with extended reaction times, but ether, ester, and amide bonds tend to hydrolyze with elevated temperature.^{42, 43} Accordingly, the TON values in **Table 1** align with the bond-hydrolysis

priority. However, assessing the influence of the "Click chemistry" strategy on catalyst stability remains challenging due to uncertainties regarding the hydrolysis of triazoles.

In addition to TON, TOF serves as an indicator of catalyst activation, and several excellent entries in literature have achieved TOF values surpassing 90 h⁻¹ (Entry 5, 6, 8, 9, 10, 11). In this work, the TOF also remains relatively high at 107.5 h⁻¹ (Entry 12), indicating that both its TON and TOF are suitable for scaling up the continuous aerobic oxidation of alcohols.

4. Conclusions

In summary, a novel carbonylation strategy utilizing ozone treatment has been successfully implemented on the surface of AC. Moreover, an innovative approach involving reductive amination has been employed to immobilize TEMPO, resulting in the development of a heterogeneous TEMPO catalyst based on AC. Various characterizations, including XPS, TGA, EPR, among others, provide evidence supporting the prosperous surface-carbonylation on AC and the covalent grafting of TEMPO. Regarding catalytic performance, the immobilized TEMPO catalysts derived from batch ozone bubbling treatment have demonstrated higher TON value reaching 1465.0. This value is much higher than those reported for similar catalysts in literature (see **Table 1**, TON: 20-1160.6), further enhancing the durability and the potential for industrial application. Additionally, the catalysts obtained from continuous ozone gas-liquid treatment exhibit slightly inferior performance compared to the bubbling treatment, this method offers the advantage of continuous reaction and facile scalability. These advantages are of significant importance in promoting the industrial application of this catalyst.

Conflicts of interest

There are no conflicts to declare.

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