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A Bifunctional Iron Nanocomposite Catalyst for Efficient Oxidation of Alkenes to Ketones and 1,2-Diketones

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Abstract

We herein report the fabrication of a bifunctional iron nanocomposite catalyst, in which two catalytically active sites of Fe-N_x and Fe phosphate, as oxidation and Lewis acid sites, were simultaneously integrated into a hierarchical N,P-dual doped porous carbon. As a bifunctional catalyst, it exhibited high efficiency for direct oxidative cleavage of alkenes into ketones or their oxidation into 1,2-diketones with a broad substrate scope and high functional group tolerance using TBHP as the oxidant in water under mild reaction conditions. Furthermore, it could be easily recovered for successive recycles without appreciable loss of activity. Mechanistic studies disclose

that the direct oxidation of alkenes proceeds via the formation of an epoxide as intermediate followed by either acid-catalyzed Meinwald rearrangement to give ketones with one carbon shorter or nucleophilic ring-opening to generate 1,2-diketones in a cascade manner. This study not only opens up a fancy pathway in the rational design of Fe-N-C catalysts, but also offers a simple and efficient method for accessing industrially important ketones and 1,2-diketones from alkenes in a cost-effective and environmentally benign fashion.

1. Introduction

Ketones, including 1,2-diketones, are very important and useful intermediates or building block in synthetic organic chemistry, pharmaceuticals, agrochemicals, and bulk/fine chemicals.^[1] Whilst many methods have been developed for the preparation of ketones, those that employ alkenes as the substrate are particularly appealing, as they are one of the most fundamental and most easily accessible chemicals. Indeed, alkenes have been used as starting materials for the synthesis of ketones over the past decades. However, only a handful of examples have been reported to date of preparing ketones and 1,2-diketones from *trans*-disubstituted alkenes via catalytic oxidation (Scheme 1).^[2,3] Furthermore, the methods developed generally suffer from such disadvantages as limited alkene scope, cost and toxicity of the metal catalysts and/or oxidants, and difficult product/catalyst separation, and environmental compatibility. Therefore, it is highly desirable to develop new approaches for the oxidation of alkenes into ketones and 1,2-diketones in a cost-effective and environmentally benign manner.

It has been well-documented that epoxides can be transformed into ketones, 1,2-diols, 1,2diketones, carboxylic acids, or other novel molecules via either facile C-O cleavage or challenging C-C bond cleavage under various conditions, such as the nucleophilic ring-opening to generate 2hydroxyalkylated derivatives,^[4] the acid-catalyzed Meinwald rearrangements to yield carbonyl

compounds,^[5] or the strong base-promoted isomerization to give allylic alcohols.^[6] Considering epoxides are readily available form alkenes via a one-step oxidation process,^[7] we thought that direct oxidation of alkenes to afford ketones and/or 1,2-diketones might be realized in a cascade manner via the formation of epoxides as an intermediate followed by acid/base catalysis or nucleophilic ring-opening (Scheme 1).

Previous works:



• Switchable reaction pathways

Scheme 1. Synthesis of ketones and 1,2-diketones from oxidation of alkenes.

The key to this strategy is the rational design and preparation of a bifunctional catalyst, in which active redox and acid/basic sites are integrated into a single catalyst to cooperatively enable the cascade epoxidation and ring-opening reactions in a sequential manner. Two such proof-of-

concept catalysts have been reported and demonstrated the potential for the reaction.^[2a,2b] However, they suffer from the issues of restricted substrate scope, demanding reaction conditions and low catalyst stability, which significantly impede their practicability in chemical synthesis. Therefore, a more efficient bifunctional catalyst, ideally heterogeneous one, which allows for the oxidation of alkenes into ketones with high activity and productivity, expanded scope, easy catalyst/product separation, and milder reaction conditions, is urgently needed.

Herein, we report a facile and easily scalable method to prepare a bifunctional iron nanocomposite, in which two catalytically active iron species, i.e. Fe-N_x and FePO₄, as redox and Lewis acid sites co-exist on the surface of hierarchical N,P-dual doped porous carbon. With inexpensive and biocompatible iron as the active sites, the nanocomposite enables synergistically cooperative catalysis for the oxidation of various alkenes into ketones and 1,2-diketones in high yields with tert-butyl hydroperoxide (TBHP) as the oxidant in water or a CH_3CN -water mixture under mild reaction conditions. Furthermore, the catalyst can be readily recovered for reuse without appreciable loss of catalytic performance.

2. Catalyst Preparation and Characterization.

2.1 Catalyst Preparation. The iron nanocomposite catalysts were prepared in a facile and environmentally benign manner, following our recently developed method that starts from naturally available and renewable biomass as nitrogen and carbon sources (see Supporting Information for the details).^[8] Typically, fresh bamboo shoots were first cut into slices, dried, and grounded into powder, followed by a hydrothermal process. The resulting solids were homogeneously mixed with $Fe(NO_3)_3$ and PPh₃, as Fe and P sources, respectively, followed by pyrolysis under a N₂ atmosphere at varying temperatures to obtain the iron nanocomposites catalysts, hereinafter denoted as Fe@NPC-T (where T represents the pyrolysis temperature, e.g.,

700, 800, and 900 °C). The iron contents were determined to be 5.0 wt% for Fe@NPC-700, 5.8 wt% for Fe@NPC-800, and 7.0 wt% for Fe@NPC-900, respectively, by the coupled plasma optical emission spectrometry (ICP-OES) (Table S2).

2.2 Catalyst Characterization. The transmission electron microscope (TEM) and highresolution images (Figure 1A-I) for the catalysts Fe@NPC-T show that metallic iron nanoparticles (NPs) containing Fe and/or Fe₃C crystalline phases with uniform size were evenly dispersed on graphitic carbon. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive X-ray (EDX) maps (Figure 1J) reveal that Fe, N, P, O and C atoms are homogeneously distributed as well. X-ray diffraction (XRD) patterns (Figure S1A) and magnetic measurements (Figure S2) verify that the metallic Fe and/or Fe₃C NPs were supported on graphitic carbon. Two characteristic D and G bands at 1590 and 1350 cm⁻¹ in Raman spectra (Figure S1B) provided solid evidence for the formation of graphitic carbon with a certain degree of graphitization and varying defected sites.^[8] N₂ adsorption/desorption measurements demonstrate that the catalysts Fe@NPC-T possess hierarchically micro-, meso-, and macropores with high specific surface areas and large pore volumes (Figure S3 and Table S1, S2).





Figure 1. (A, B) TEM images of Fe@NPC-700, (C) HR-TEM image of Fe@NPC-700; (D, E) TEM images of Fe@NPC-800, (F) HR-TEM image of Fe@NPC-800; (G, H) TEM images of Fe@NPC-900, (I) HR-TEM image of Fe@NPC-900; (J) HAADF STEM image and corresponding EDX mappings of Fe, N, O, and P of Fe@NPC-800.

The nature of N, P, and Fe in Fe@NPC-T was studied by X-ray photoelectron spectroscopy (XPS; Figure 2a and 2b, Figure S4). The N 1s spectrum contains 5 peaks at 398.02, 399.6, 400.4, 401.3, and 402.5 eV, which are assigned to pyridinic, Fe-N_x, pyrrolic, quaternary, and oxidized N, respectively (Figure 2a). The content of each type of nitrogen varies as the pyrolysis temperature increases (Table S3). Of the peaks, the one at 399.6 eV is in good consistence with that of ironphthalocyanine (FePc), indicating that Fe coordinates with N atoms in aromatics to form catalytically active Fe-N_x sites.^[9] This observation also clearly suggests the N atoms are incorporated into the carbon lattice. Three types of P species could be identified from the P 2p spectrum, that is, Fe-P (zero valence state, 129.2 and 130.4 eV),^[10] P-C (132.8 eV),^[8d, 11] PO₃⁻ and PO_4^{3-} (5+, 133.7 and 134.4 eV)^[11] (Figure S4). The formation of FePO₄ was further supported by FT-IR experiment with appearance of a characteristic band at 1045 cm⁻¹, assignable to the stretching of the P-O bond present in PO₄³⁻ (Figure S7).^[12] The Fe 2p XPS spectrum (Figure 2b) were fitted into three peaks at 706.8, 710.4, and 712.0 eV, respectively. The peak at 706.8 eV can be attributed to zero valence Fe (metallic iron or carbide).^[9b, 13] The peak at 710.4 eV can be assigned to Fe in Fe-N_x configuration, while the peak at 712.0 eV can be indexed to Fe³⁺ in FePO₄.^[14] A notable positive shift in binding energy assignable to Fe-N_x configuration in Fe@NPC-T compared with that of FePc implies interactions of Fe-N_x with metallic iron NPs.^[9b] Noticeably, the content for each iron species in the Fe@NPC-T varies with pyrolysis temperatures.



Figure 2. High-resolution XPS spectra of N 1s (a) and Fe 2p (b) for Fe@NPC-700, 800 and 900; Fe *K*-edge XANES (c) and Fourier transform (FT) EXAFS (d) spectra of Fe@NPC-700, 800 and 900, with FePc, Fe foil, and FePO₄ as references.

X-ray absorption measurements were further performed to analyze the coordination environment of Fe at the atomic level. The near-edge absorption energy position of Fe@NPC-T was located between that of Fe foil and FePO₄ in Fe K-edge absorption near-edge structure (XANES) suggests that the valence state of Fe is in between 0 and +3 (Figure 2c). This is in agreement with the XPS results. The Fourier transform (FT) k^3 -weighted EXAFS spectra of

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Fe@NPC-T show one main peak at around 1.5 Å, which belongs to the first coordination shell of Fe-N and is notably similar to that of FePc, suggesting that they are more likely to form Fe-N_x coordination structures (Figure 2d).^[9b, 15] Besides, the peak at around 2.5 Å, ascribed to the Fe-C distance of the second neighbor shell was also observed.^[9b] However, the spectrum of Fe@NPC-700 is more similar to Fe foil with two strong peaks at around 2.1 and 4.5 Å, which correspond to the Fe-Fe distance,^[9b] revealing the presence of metallic iron crystalline structures. The peak of the Fe-Fe bond could also be observed in Fe@NPC-800 and Fe@NPC-900, corroborating that metallic iron exists in both samples, which are consistent with the HR-TEM and XRD results. Noticeably, the EXAFS spectrum of Fe@NPC-800 or Fe@NPC-900 shows a higher peak intensity for Fe-N bonding and a lower intensity for Fe-Fe bonding compared to that of Fe@NPC-700. Nonetheless, these data suggest that Fe-N_x configurations are incorporated in the graphitic carbon frameworks in the catalysts and their intensity increases with the increase of pyrolysis temperatures.

3. Results and discussion

3.1 Oxidation of Alkenes to Ketones. To examine the catalytic activity of the iron nanocomposite Fe@NPC-T for the oxidative cleavage of alkenes, *trans*-stilbene **1a** was chosen as a model substrate (Table 1). The reaction was performed in the presence of Fe-@NPC-800 as a catalyst and 5 equivalents of TBHP as an oxidant at 100 °C in water. To our delight, full conversion of **1a** with formation of one-carbon shorter benzophenone **2a** as major product in 86% selectivity was observed (entry 1). The selectivity to **2a** as high as 92% could be achieved with 98% conversion of **1a** at 90 °C under otherwise identical conditions (entry 2). However, a further decrease of reaction temperature to 80 °C led to a rather lower reactivity (entry 3). Lowering the amount of TBHP (e.g., 3 equivalents with respect to **1a**) drastically decreased the reactivity too

(entry 4). Using hydrogen peroxide, air, or molecular oxygen instead of TBHP as terminal oxidant, no reaction was observed with full recovery of **1a** under identical conditions (entries 5-7). Further screening of the as-prepared catalysts, e.g., Fe@NPC-700 and Fe@NPC-900, reveal that the pyrolysis temperature for preparation of the iron nanocomposite has an important influence on the reactivity (entries 8 and 9), with Fe@NPC-800 affording the best result. Control experiments employing commercially available Fe₂O₃, Fe₃O₄, Fe(NO₃)₃, FePO₄, iron phthalocyanine (FePc), and nano Fe powder as catalysts for the reaction all show inferior reactivity with formation of a mixture of products (entries 11-16). In addition, when NPC-800 without the introduction of iron was employed as a catalyst, no reaction was observed under the same conditions, indicating the essential role of the Fe@NPC-T in catalysis (entry 17). Therefore, the optimized conditions are as follows: Fe@NPC-800 as a catalyst, TBHP (5 equivalents with respect to *trans*-stilbene) as an oxidant, 90 °C in water. Of note, the carbon balance closure is nearly 90% for the benchmark reaction under different conditions, as shown in Table S9.

Table 1. Optimization of reaction conditions for synthesis of ketones.^a



1	Fe@NPC-800	TBHP	100	100	86	0	10	0
2	Fe@NPC-800	ТВНР	90	98	92	0	4	2
3	Fe@NPC-800	TBHP	80	57	65	12	14	9
4 ^c	Fe@NPC-800	TBHP	90	43	91	0	9	0
5	Fe@NPC-800	H_2O_2	90	0	-	-	-	-
6	Fe@NPC-800	Air	90	0	-	-	-	-
7 ^d	Fe@NPC-800	O ₂	90	0	-	-	-	-
8	Fe@NPC-700	TBHP	90	79	42	47	11	0
9	Fe@NPC-900	TBHP	90	100	71	10	11	0
10	Fe@NC-800	TBHP	90	90	59	24	17	0
11	Fe_2O_3	TBHP	90	19	32	68	0	0
12	Fe_3O_4	TBHP	90	23	30	48	22	0
13	Fe powder	TBHP	90	11	45	28	27	0
14	Fe(NO ₃) ₃	TBHP	90	7	71	29	0	0
15	FePc	TBHP	90	31	41	37	22	0
16	FePO ₄	TBHP	90	11	77	7	16	0
17	NPC-800	TBHP	90	0	-	-	-	-

^{*a*}Reaction conditions: *trans*-stilbene (0.2 mmol), catalyst (10 mol% of Fe), oxidant (5 eq.), H₂O (4 mL), 90 °C, 12 h. ^{*b*}Determined by GC-MS. ^{*c*}3 eq. TBHP. ^{*d*}Oxygen balloon.

After identifying the optimal reaction conditions, we next investigated the generality of this protocol as shown in Table 2. Overall, a variety of alkenes could efficiently undergo the selective cleavage reaction to afford their corresponding one-carbon shorter ketones in high yields with good tolerance of various functional groups. Electron donating group-substituted 1,2-diarylalkenes gave higher yields than those substituted by electron-withdrawing groups, e.g., -NO₂ (1i), -CN (1j, 1k), and -CF₃ (1l). Halogen-substituted 1,2-diarylalkenes (1b-e) tolerate the present conditions and the respective diaryl ketones were achieved in 80-87% yields with no undesired dehalogenation taking place. Other functional groups, e.g., PhthN- (1m), -NH₂ (1n), -COOH (1o), and MeO₂C- (1p), were also compatible with the present conditions. Delightfully, 2,3,4,5,6-

pentafluoro-substituted 1,2-diarylalkene (1r) also worked well to produce 2,3,4,5,6pentafluorobenzophenone with a decent yield, which is frequently used in the synthesis of OLED^[16] and F-containing polymers.^[17] More importantly, heterocycle-substituted internal alkenes, such as 2-styrylthiophene (1t) and 2-styrylpyridine (1s), are compatible with this catalytic system, delivering their respective ketones in 71% and 77% yield, respectively. These results indicate that this method is highly useful for the preparation of pharmaceuticals and functional materials. Furthermore, aryl and alkyl-substituted unsymmetric alkenes (1u-z) could undergo the oxidative cleavage reaction to selectively produce their corresponding ketones in good yields under the optimized conditions. In addition, various substituted styrenes (1ab-ae) work well to produce its corresponding aldehyde as the final product. For those 1,1-disubstituted terminal alkenes, e.g., ethene-1,1,2-trivitribenzene (1af), (E)-prop-1-ene-1,2-dividibenzene (1ag), and 1,1,2-trisubstituted alkenes, e.g., ethene-1,1-dividibenzene (1ah), prop-1-en-2-ylbenzene (1ai), they were converted into their corresponding one-carbon shorter ketones and tertiary alcohols (2afag) in satisfactory yields, respectively. However, for dialkyl substituted alkene, e.g., 2-octene (1aa), a mixture of its corresponding epoxide, aldehyde and acid was observed with no formation of the desired ketone, mainly due to the higher oxidation potential of aliphatic acids than benzyl carboxylic acids, which is unfavourable for the oxidative decarboxylation of aliphatic acids to the corresponding carbon radical and subsequent cascade oxidation process.^[18]

Table 2. Substrate scope of alkenes for synthesis of ketones.^a

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^{*a*}Reaction conditions: alkene (0.2 mmol), catalyst (10 mol% of Fe), TBHP 70 wt% in water (5 eq.), H₂O (4 mL), 90 °C, 12 h. ^{*b*}No detected. ^{*c*}*cis*-stilbene was used instead. Yields of isolated product are reported.

3.2 Oxidation of Alkenes to 1,2-Diketones. In the course of the condition optimization for the reaction of *trans*-stilbene **1a** catalyzed by Fe@NPC-800, benzil (**5a**) was detected, albeit with considerably lower yield (Table 1, entries 2 and 3). This finding indicates that 1,2-diketones could be synthesized from alkenes if appropriate conditions are in place. Therefore, we attempted to synthesize 1,2-diketones from alkenes under the catalysis of Fe@NPC-800 by modification of the reaction conditions.

With **1a** still as the model substrate, a set of parameters including solvent, additive, temperature, and oxidant were intensively screened, and the results are compiled in Table S6 and Figure S11. To our pleasing, in the presence of 30 mol% of TBAI, 83% of isolated yield to benzil **5a** was achieved using Fe@NPC-800 (10 mol% of Fe) as a catalyst, 5 equivalents of TBHP as an oxidant (with respect to **1a**), CH₃CN/H₂O (15/1, v/v) as solvent at 90 °C. Note that TBAI was employed as an additive because of the well-known capacity of iodide as a good nucleophilic and leaving group.^[3e,3f,19]

With the optimized conditions in hand, we subsequently explored the generality of this method to selectively convert various alkenes to into 1,2-diketones. As shown in Table 3, all the stilbenes examined could be efficiently converted to their corresponding 1,2-diketones in high yields. A variety of functional groups, such as halides (**1b-d**), Me- (**1e**), MeO- (**1g** and **1h**), -CN(**1j** and **1k**), CF₃- (**11**), and NO₂- (**1i**), MeO₂C- (**1p**) are all tolerated. 2,3,4,5,6-pentafluoro-substituted 1,2-diarylalkene (**1r**) also worked well to produce **5m** in satisfactory yield. (E)-2-styrylnaphthalene (**1q**) and heteroatom-containing alkene, 2-styrylthiophene (**1t**), were efficiently

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converted to their corresponding 1,2-diketones in high yields. Notably, 1-((E)-2-(cyclohexa-1,5dien-1-yl)vinyl)-4-((E)-styryl)benzene (10) containing two C=C bonds was smoothly oxidized into 50 in 74% yield with 10 equivalent of TBHP and 24 h. Aryl and alkyl-substituted unsymmetric alkenes (1q', 1r', 1u, 1x-z) also worked well to deliver their respective 1,2-diketones in 57-81% yields. More surprisingly, styrene (1w') was directly oxidized into phenylglyoxylic acid (PGA) 5w in 57% yield, a key building block for wide applications in synthesis of a-amino acids, pharmaceuticals, and agrochemicals,^[20] which still remains a challenge in organic synthesis from readily available starting materials under facile and sustainable conditions. 1,1-disubstituted alkenes (1x' and 1y') could be converted into the corresponding α -hydroxyl-acid (5x and 5y) in 51% and 45% yields, respectively. Likewise, cycloalkenes and aliphatic alkenes, such as, cyclohexene $(1z^2)$, and 2-octene $(1aa^2)$, are also suitable as substrates for the oxidation to 1,2diketones. For the terminal aliphatic alkene, vinylcyclohexane (1ab), was also oxidized into aketo acid 5ab in decent yield. Note that, 2-hydroxycyclohex-2-en-1-one (5z) was obtained via the isomerization of cyclohexane-1,2-dione. The α -hydroxyl-ketones (**5ac** and **5ad**) were obtained in moderate yields when using 1,1,2-trisunstituted alkenes (1ac' and 1ad') as substrates instead. In addition, several biologically active natural derivatives containing C=C bond, e.g., Camphor (1ae'), Resveratrol (1af'), Pterostilbene (1ag'), and Polydatin (1ah'), can be efficiently oxidized into their respective 1,2-diketones in high yields. Overall, this method demonstrates a great substrate scope, highlighting its practical utility for direct synthesis of benzils from alkenes under mild and sustainable reaction conditions.

 Table 3. Substrate scopes of alkenes for synthesis of 1,2-diketones.



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^{*a*}Reaction conditions: alkene (0.2 mmol), Fe @NPC-800 (10 mol% of Fe), TBHP 70 wt% in water (5 eq.), TBAI (22.1 mg, 30 mol%), CH₃CN/H₂O (2 mL, v/v = 15/1), 90 °C, 12 h. ^{*b*}TBHP 70 wt% in water (10 eq.), 24 h. ^{*c*}Isomerization product was obtained. Yields of isolated product are reported.

To further explore the applicability of this method, we carried out a one-pot cascade reaction starting from alkenes for synthesis of biologically active heterocyclic compounds, such as 2,3-diphenylquinoxaline (**6a**) and 2,4,5-triphenyl-1H-imidazole (**6b**) (Scheme 2), because 1,2-diketones are well-known building blocks for such constructions.^[21] After the full conversion of *trans*-stilbene under the optimized conditions, benzene-1,2-diamine or benzyl aldehyde/NH₄OAc was directly added into the reaction mixture for sequential condensation cyclization. To our delight, **6a** and **6b** were isolated in 87 and 67% yields, respectively. Comparatively, a considerable lower reactivity was achieved when the condensation was performed directly starting from benzil **5a** in the absence of the catalyst Fe@NPC-800 under otherwise identical conditions (Scheme S2). Such a finding is in line with previous reports ^[21c-f] and clearly indicates that the catalyst Fe@NPC-800 with Lewis acid sites could greatly facilitate the condensation, further highlighting its expanded potential.



Scheme 2. Applicability of one-pot cascade reaction for synthesis of heterocycles starting from alkene.

3.3 Stability of the Catalyst Fe@NPC-800. The stability and reusability of the catalyst Fe@NPC-800 was also investigated. Upon completion of the benchmark oxidation reaction, the Fe@NPC-800 catalyst was easily separated from the product and recollected via centrifugation, and after washing and drying, it was used in subsequent cycles. As shown in Figure S13 in the Supporting Information, the catalyst exhibited good stability and could be easily separated and reused at least 6 times without significant loss of both the activity and selectivity, strongly indicating its robust stability.

3.4 Relationship between Catalytic Performance and Properties of the Catalyst. To better understand the reaction pathway of the oxidative cleavage of alkenes into a class of important ketones with one-carbon shorter, the benchmark reaction under the optimized conditions was further investigated. The product distribution as a function of reaction time as shown in Figure 3 discloses that the epoxidation of *trans*-stilbene **1a** with TBHP to produce epoxide **3a** dominates the reaction at the early stage in the presence of Fe@NPC-800 (within 1 h), accompanied with concomitant formation of diphenylacetaldehyde (**7a**) and benzophenone (**2a**). This may not be surprising because the Fe-N_x sites are key species in Fe@NPC-800, which structurally mimics Feporphyrin complexes and have been well-documented to efficiently enable alkene epoxidation.^[22] With an elapse of reaction times, **1a** was consumed quickly, and the formation of benzophenone **2a** prevailed accompanied with the gradual conversion of both **3a** and **7a**. We subsequently correlated the content of Fe-N_x sites in the as-prepared catalysts Fe@NPC-T (T = 700, 800, and 900°C) and the catalytic activities as shown in Table S8, and found that the conversion of *trans*-stilbene **1a** highly depends on the content of Fe-N_x sites under otherwise identical conditions,

indicating that Fe-N_x is indeed catalytically active sites for the oxidation of alkenes in the present catalytic system.



Figure 3. Product distribution of oxidation of *trans*-stilbene as a function of reaction times under

the optimized conditions.



Figure 4. Pyridine-adsorption FT-IR spectra on the catalyst Fe@NPC-800 observed at varying temperatures.

Interestingly, diphenylacetaldehyde 7a as an intermediate was detected during the reaction course. This is reminiscent of the well-known Meinwald rearrangement of epoxide in the presence of acid.^[5] As such, pyridine-adsorption FT-IR experiment for the catalyst Fe@NPC-800 was conducted. As shown in Figure 4, the spectrum discloses the presence of Lewis acid sites on the catalyst, with appearance of a characteristic peak at 1450 cm⁻¹ and its concentration as high as 267.6μ mol per gram (Table S5), which most likely stem from the high valence of iron in FePO₄. Pyridine-poisoning experiment (Table S7) shows a considerable decrease of reactivity with 52% conversion of 1a, with maintaining 3a remaining as the major product due to the loss of the concentration of acid sites on the catalyst. Investigation on the catalytic activity and product selectivity (or distribution) over the catalysts Fe@NPC-700 and Fe@NPC-900 with different concentration of Lewis acid sites also gave similar results (Table 1, Table S8, and Figure S9), that is, higher conversion of 1a with higher content of Fe-N_x sites, while better selectivity to 2a with higher concentration of acid sites. This finding not only supports the presence of acid sites in the catalyst; but more importantly it indicates that the acid sites exert a critical effect on reaction efficiency and product selectivity. For comparison, the catalyst Fe@NC-800 without introduction of P was prepared according to the same preparation method, which gave a relatively lower reactivity, and especially an inferior selectivity to 2a under otherwise identical reaction conditions (Figure S9). The pyridine-adsorption FT-IR experiment also discloses that the Fe@NC-800 catalyst processes a relatively stronger concentration of Lewis acid sites (Figure S8 and Table S5). Such observations confirm that the addition of PPh_3 could facilitate the formation of $FePO_4$, giving rise to the Lewis acid sites. Further studies show that the reaction activity and selectivity to

benzophenone follows a volcanic trend when varying the added amount of PPh₃ for catalyst preparation, with the 20 wt% loading giving the best catalytic activity (Figure S10).



Scheme 3. Proposed mechanism for oxidation of alkenes to ketones and 1,2-diketones.

3.5 Mechanistic Studies. Based on the results discussed above, we proposed a plausible reaction pathway as shown in Scheme 3. Firstly, an alkene is epoxidized by the Fe@NPC-800 catalyst with TBHP to generate an epoxide. Subsequently, the epoxide is converted to ketone with one-carbon shorter, in which sequential reactions take place, involving (i) a Lewis acid-catalyzed Meinwald rearrangement of the epoxide to an α-disubstituted acetaldehyde, and (ii) oxidation of the aldehyde to a disubstituted acetic acid, (iii) decarboxylation of the acid with loss of one carbon

atom followed by one-electron oxidation of the resulting radical, and (iv) attach at the carbon cation by water as nucleophile and further oxidation to produce a ketone.

To gain more evidence for this mechanism, a set of control experiments were subsequently carried out (Scheme 4). Stilbene epoxide 3a could be efficiently converted towards benzophenone 2a in 92% GC yield (84% isolated yield) under the optimized conditions (Scheme 4 eq. a); but in the absence of TBHP under otherwise identical conditions, only 53% conversion of **3a** was achieved, affording Meinwald rearranged product diphenylacetaldehyde 7a in 49% GC yield (Scheme 4 eq. b). This observation indicates that TBHP as oxidant could accelerate selective conversion of epoxide to the desired ketones. Next, diphenylacetic acid **6a**, which is readily formed from oxidation of diphenylacetaldehyde 7a, could also be effectively transferred into 2a in 89% GC yield together with 11% of 1.2-diphenylmethanol and evolution of a CO₂ molecule (confirmed by GC analysis) (Scheme 4 eq. c). As is known, diphenylacetic acid can easily undergo oxidative decarboxylation into benzyl radical with release of CO₂.^[18] In the presence of an oxidant, the generated benzyl radical can be oxidized to carbocation, which can be easily attacked by a nucleophile like H_2O to form an alcohol and further oxidized into ketone. To prove this, $H_2^{18}O$ labelling experiment was performed (Scheme 4 eq. d and Figure S12). No appreciable difference in reactivity could be observed, and 96% of isolated yield of benzophenone was obtained with 100% ¹⁸O labeling. Besides, 4% of diphenylmethanol with 100% ¹⁸O labeling was also detected. This finding not only demonstrates that the origin of oxygen atom in benzophenone and 1,2diphenylmethanol stems from water rather than TBHP, but further proves that water indeed participates in the reaction as a nucleophile to attack the in-situ generated decarboxylated intermediate (Scheme 3). Taking into account all these control experimental results, we may safely

conclude that the proposed reaction pathway is most likely to be operative in our catalytic system (Scheme 3, path I).



Scheme 4. Control experiments for the synthesis of ketones.

On the other hand, a competitive pathway of nucleophilic substitution prior to the Meinwald rearrangment is also possible if a strong nucleophile presents during the ring-opening of epoxide catalyzed by Lewis acid. If this is the case, the reaction would proceed following the pathway as shown in Scheme 3, path II. To investigate the possibility, new control experiments were conducted (Scheme 5). Firstly, using 2-iodo-1,2-diphenylethan-1-one **A** as the substrate for the reaction under the optimized conditions (Scheme 5 eq. a), nearly quantitative yield to benzil **5a** was observed. The iodide in **A**, as a good leaving group, can be readily substituted by water to produce 2-hydroxy-1,2-diphenylethan-1-one **B** in CH₃CN/H₂O mixture at 90°C (Scheme 5 eq. b), which can be quantitatively converted into **5a** under the optimized conditions (Scheme 5 eq. c). In contrast, a considerably lower reactivity was observed when **A** was subjected to the optimized

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conditions in the absence of water (Scheme 5 eq. d), indicating that H_2O as a nucleophile is favorable for the reaction process. Taken all the results together, we consider that the proposed reaction pathway as illustrated in Scheme 3, path II is feasible.



Scheme 5. Control experiments for the synthesis of 1,2-diketones.

4. Conclusions

In conclusion, we have developed a novel, inexpensive bifunctional iron nanocomposite catalyst in a facile and environmentally friendly manner. Two key iron species, Fe-N_x and FePO₄ as the oxidation and acid sites, respectively, were simultaneously integrated on the hierarchical porous carbon, which are primarily responsible for the direct oxidative cleavage of alkenes via the formation of epoxide as the key intermediate. A broad range of alkenes could be efficiently

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converted into industrially important ketones and 1,2-diketones with good tolerance of functional groups using TBHP as the oxidant under mild reaction conditions. In addition, the catalyst can be readily recovered for successive recycles. This study provides a simple and efficient method for the synthesis of synthetically significant ketones and 1,2-diketones from the direct oxidation of alkenes in a cost-effective and environmentally friendly manner, and we believe the method should be very useful in the synthesis of fine chemicals, pharmaceuticals, agrochemicals and materials.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

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Raman spectra; N₂ sorption isotherms and pore size distribution; XRD pattern; Ni 2p, P 2p, N 1s, and C 1s XPS spectra for Fe@NPC-700, Fe @NPC-800, and Fe@NPC-900; chemical composition and texture properties of Fe@NPC-700, Fe @NPC-800, and Fe@NPC-900. ¹H and ¹³C NMR spectroscopy data for all obtained products.

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Bifunctional Catalysis: Both active sites of Fe-N_x and FePO_4 on N,P-codoped carbon facilitate selective oxidation of alkenes.