



A study of FeN_x/C catalysts for the selective oxidation of unsaturated alcohols by molecular oxygen

Jinping Zhang^a, Shinichi Nagamatsu^b, Junmou Du^a, Chaoli Tong^a, Huihuang Fang^a, Dehui Deng^{a,c}, Xi Liu^d, Kiyotaka Asakura^{b,*}, Youzhu Yuan^{a,*}

^a State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols–Ethers–Esters, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

^b Institute for Catalysis, Hokkaido University, Kita 21, Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

^c State Key Laboratory of Catalysis, iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^d Synfuels China Technology Co., Ltd., Beijing 101407, China

ARTICLE INFO

Article history:

Received 1 April 2018

Revised 1 August 2018

Accepted 2 August 2018

Available online 7 September 2018

Keywords:

FeN_x/C catalysts

Selective oxidation

Unsaturated alcohol

Characterization

Regeneration

ABSTRACT

Transition-metal nitrides can exhibit catalytic performance comparable to that of noble metal catalysts in many reactions. However, investigations on the correlation of catalyst structure, performance, and stability are still highly demanded. Here, a series of metal nitrides were prepared and evaluated for the selective oxidation of alcohols by molecular oxygen. Among them, FeN_x/C-*T* catalysts (*T* represents the pyrolysis temperature) display above 95% selectivity to the corresponding aldehydes in the selective oxidation of unsaturated alcohols. The optimized FeN_x/C-900 catalyst gives the highest TOF of 7.0 h^{−1} for the conversion of 5-hydroxymethylfurfural to 2,5-diformylfuran. A combination of characterizations and experiments suggests that Fe–N₄ species are the main active sites. In addition, we investigate the reasons for the catalyst deactivation and provide an effective approach to regenerating the catalysts. The results indicate that the deactivated catalysts can be regenerated by heat treatment under NH₃/N₂ after each run. Based on these studies, a plausible reaction mechanism over the FeN_x/C catalysts is proposed.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

In recent years, metal nitride catalysts have been developed rapidly in the fields of electrochemistry [1–3], catalytic oxidation [4–6], and organic synthesis [7] because of their unique structure properties. Metal nitride catalysts are often prepared by calcining different precursors obtained from template methods [6,8], ball milling [1,4], and oxidative polymerization [2,9]. Deng et al. reported a graphene-supported FeN₄ (an iron moiety coordinated with four nitrogen groups) catalyst synthesized by ball milling and calcination. It achieved the oxidation of benzene using H₂O₂ as oxidant with 23.4% conversion and 18.7% yield of phenol at room temperature over 24 h [4]. Li and co-workers demonstrated that a N-doped graphene-supported cobalt catalyst could convert benzyl alcohol to benzaldehyde under O₂ with a yield of 92.4% after 5 h at 130 °C [5]. Xie et al. proposed an Fe–N–C catalyst using a template method, which was active for the oxidative dehydrogenation of 5-hydroxymethylfurfural (HMF) in aerobic solution with

only a 40% yield of 2,5-diformylfuran (DFF) over 8 h at 80 °C under 1.0 MPa O₂ [8]. Quite recently, Liu et al. prepared atomically dispersed Fe–N–C catalysts at high temperature using MgO nanoparticles as the template. The Fe–N–C-700 catalyst exhibited high activity for the selective oxidation of C–H bonds using *tert*-butyl hydroperoxide (TBHP) as an oxidant [6].

Despite considerable studies of metal nitrides, the structure of active sites and stability still deserve further investigation. The difficulties in investigating the active phases mainly lie in the complexities of structure and uncertainties of catalyst composition. To date, no consensus on the correlation of catalyst structure, performance, and stability has been achieved in the literature. Much researches has been conducted on active sites of iron-based nitrides for the oxygen reduction reaction (ORR) [1,10,11]. Artyushkova et al. proposed that a pyrrolic N species acted as the active site for O₂ reduction to H₂O₂ and that Fe–N_x species and pyridinic N atoms were the active sites for H₂O₂ reduction to H₂O [10]. Choi and co-workers reported that FeN_xC_y moieties were the main active sites for H₂O₂ reduction [11]. Further, recent work by Liu et al. discriminated the form of active sites in the Fe–N–C catalysts. They verified that the Fe^{III}–N₅ entity is the main active site for the selective oxidation of C–H bonds with TBHP [6].

* Corresponding authors.

E-mail addresses: askr@cat.hokudai.ac.jp (K. Asakura), yzyuan@xmu.edu.cn (Y. Yuan).

On the other hand, the stability of metal nitride catalysts has faced great challenges. Previous work proved that Fe–N₄ and Fe–N–C catalysts were deactivated in the oxidation reaction even at room temperature [4,8]. Deactivation phenomena also occurred in the ORR system [1,4,8,12,13]. Thus, it is very important to probe the essence of catalyst deactivation. A detailed study of deactivated catalysts will promote the development of methods to regenerate their performance.

It is well known that the selective oxidation of alcohols is an important organic reaction that plays a huge role in industrial applications, such as energy conversion and storage [14–18], the production of fine chemicals [15,17], and biomedical manufacturing [16,18]. Many catalysts have been reported for such reactions, such as supported Au [19–22] and Pt-group (Pt, Pd, and Ru) [23–27] catalysts, and other non-precious-metal catalysts [28–37]. In this work, we have prepared a series of metal nitrides (M_{N_x}/C-*T*, M = Fe, Co, Cu, Cr, and Ni; *T* represents the different pyrolysis temperatures) by two-step pyrolysis treatment and employed them for the selective oxidation of several alcohols by O₂, aiming to investigate the active phase, stability, and regeneration of metal nitrides in the process of selective oxidation of alcohols. The results indicate that the FeN_x/C-*T* catalysts exhibit superior activity and selectivity for the conversion of unsaturated alcohols to the corresponding aldehydes with O₂ as an oxidant. A Fe–N₄ entity is identified as the main active phase for the FeN_x/C-*T* catalysts through a combination of X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), extended X-ray absorption fine structure (EXAFS), control experiments, and poisoning experiments with potassium thiocyanate (KSCN). In addition, efforts have been made to explore the reason for deactivation and the regeneration of metal nitride catalysts.

2. Experimental

2.1. Chemicals and reagents

Multiwalled carbon nanotubes (CNTs) and carbon black (XC-72 and Ketjen black EC-600JD) were purchased from Shenzhen Nanotech Port Co. Ferric trichloride (FeCl₃·6H₂O), cobalt nitrate (Co(NO₃)₂·6H₂O), cupric nitrate (Cu(NO₃)₂·3H₂O), chromic nitrate (Cr(NO₃)₃·9H₂O), and nickel nitrate (Ni(NO₃)₂·6H₂O) were obtained from Sinopharm Chemical Reagent Co. 5-Hydroxymethylfurfural (HMF), 2,5-diformylfuran (DFF), and 2,5-furandicarboxylic acid (FDCA) were purchased from Aladdin Industrial Corporation (Shanghai, China).

2.2. Catalyst preparation

Commercial carbon materials, including CNTs, XC-72, and Ketjen black EC-600JD, were treated in HNO₃ solution at 100 °C for 16 h. The M_{N_x}/C-*T* catalysts were prepared in a two-step pyrolysis process using *m*-phenylenediamine as the nitrogen source according to the previous literature [2,9]. Briefly, *m*-phenylenediamine (3.0 g, 27.7 mmol) and the carbon support (Ketjen black EC-600JD, 0.4 g) were dispersed into a beaker containing a concentrated HCl aqueous solution. The suspension was stirred in an ice water bath, while the precooled oxidant (NH₄)₂S₂O₈ (2.0 M, 28 mL) was added slowly to oxidize *m*-phenylenediamine to cover the carbon support. After being stirred for 24 h, the suspension solution was filtered, washed, and dried to obtain the N-doped carbon support. A series of metal salts (FeCl₃·6H₂O, Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Cr(NO₃)₃·9H₂O, and Ni(NO₃)₂·6H₂O) were used as precursors. The metal salt solution (0.3 M, 10 mL) was added dropwise into the dry N-doped carbon support (1.2 g) dispersed in 20 mL of water. Then the suspension was filtered and dried in

an oven overnight at 100 °C before heat treatment. The obtained precursors were calcined at different temperatures from 600 to 1000 °C for 1 h under nitrogen. Subsequently, the pyrolyzed samples were leached in HCl solution (1 M, 100 mL) at 80 °C for 8 h to remove impurities, such as MC_x, MO_x, and MS_x, from the sample and washed to neutralize the samples using deionized water. Finally, the samples were calcined again in the same atmosphere and temperature for 3 h to form the corresponding FeN_x/C-*T*, CoN_x/C-*T*, CuN_x/C-*T*, CrN_x/C-*T*, and NiN_x/C-*T* catalysts. Similarly, FeN_x/CNT-*T* and FeN_x/XC72-*T* were synthesized by changing the carbon supports. FeN_x/C-700° and FeN_x/C-600° with the same N amount as FeN_x/C-900 were also obtained by controlling the amount of the nitrogen source. Briefly, other conditions remain unchanged, only decreasing the amount of *m*-phenylenediamine to 0.2 and 0.15 g for FeN_x/C-700° and FeN_x/C-600°, respectively. M/C-*T* and CN_x-*T* were prepared using a similar method without the addition of the nitrogen source and metal salt precursor, respectively.

2.3. Catalyst characterization

The porous properties of the catalysts were analyzed by N₂ adsorption–desorption measurements at –196 °C using a Micromeritics Tristar II 3020 apparatus. The catalysts were degassed at 100 °C for 4 h under vacuum before the measurements. The specific surface area was calculated through the Brunauer–Emmett–Teller (BET) method. The average pore diameter of the catalysts was determined by the Barrett–Joyner–Halenda (BJH) desorption isotherm. Powder X-ray diffraction (XRD) analysis was carried out on a PANalytical X'pert Pro diffractometer using CuK_α radiation (λ = 1.5418 Å) at a scanning rate of 20°/min from 10° to 90°.

Raman spectra were collected on a Renishaw Invia Raman microscope with a CCD detector. The Raman data were recorded using 532 nm excitation by a He–Cd laser source with a 10 s exposure. The output power of the laser was 13 mW.

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken on a transmission electron microscope (TECNAI F30). The acceleration voltage was 300 kV. The catalysts were ground and ultrasonically dispersed in ethanol before observation. The suspension was dropped onto a copper grid supported by superthin carbon films.

The metal content of the catalysts was obtained by an X-ray fluorescence (XRF) spectrometer (Bruker) at 60 kV and 50 mA. Before the measurements, the catalysts were mixed with boric acid (H₃BO₃) and then pressed into 2 mm pellets. The content of C, N, and H was measured by elemental analysis on an Elementar Vario EL III instrument.

XPS measurement was performed on a Qtac-100 LEISS spectrometer with an AlK_α incident radiation source. The C1s peak (284.6 eV) was referenced to calibrate the binding energies of the catalysts.

ESR spectra were recorded on an X-band Bruker EMX-10/12 apparatus at –173 °C. The samples (20 mg) were poured into quartz tubes and cooled to –173 °C in liquid nitrogen. The experimental frequency was 9.45 GHz, and the operating power was 19.94 mW.

EXAFS measurement was carried out at BL9C of the Photon Factory, Institute for Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF), Japan (Proposal 2016G546). The X-rays were monochromatized by a Si(1 1 1) double crystal. The XAFS spectra were collected at room temperature. Higher harmonics were rejected by a total-reflection focusing mirror. The ionization chambers for the incident X-rays (I₀) and the transmitted X-rays (I) were both filled with N₂. The REX program was used to analyze the EXAFS spectra (μ(E)) [38–40]. The

smoothed background ($\mu_s(E)$) was estimated by a smoothing spline method and normalized by the edge height ($\mu_0(E)$), whose energy dependence was calculated using the McMaster equation. The energy scale was converted to wavenumbers, k , using the following equation,

$$k = \sqrt{2m(E - E_0)/\hbar^2}, \quad (1)$$

where E_0 is absorption edge energy. Thus, the obtained EXAFS oscillation ($\chi(k)$) was weighted by k^3 and Fourier transformed. The peaks were filtered and inversely Fourier transformed for further curve-fitting analysis in k -space. The curve fitting analysis was carried out using the equations

$$k^3\chi(k) = \sum_i \frac{S_i N_i F_i(k)}{k r_i^2} \exp(-2k^2 \sigma_i^2) \exp\left(-\frac{2r_i}{\lambda_i}\right) \sin(2kr_i + \phi_i(k)), \quad (2)$$

$$\chi(k) = \frac{\mu(E) - \mu_s(E)}{\mu_0(E)}, \quad (3)$$

where S_i , r_i , N_i , σ_i , and λ_i are the inelastic loss factor, bond distance, coordination number, Debye–Waller factor, and mean free path of the i th bonds, respectively. The values of r_i , N_i , σ_i , and E_0 were determined by curve-fitting analysis. The value of λ_i was fixed at 7 Å and that of S_i was determined by standard compounds. For the curve-fitting analysis, the phase shift $\phi_i(k)$ and amplitude functions $F_i(k)$ of the Fe–Fe, Fe–N, Fe–C, and Fe–O shells were calculated using the FEFF program [41,42].

2.4. Catalytic test

Selective oxidation experiments with various alcohols were conducted in a high-pressure reactor. A series of alcohols (benzyl alcohol (99.5%), furfuryl alcohol (98.0%), HMF (99.0%), 5-methyl-2-furfuryl-methanol (97.0%), 2, 5-furandimethanol (97%), cyclohexanol (98.5%), glycerol (99.0%), and ethanol (99.5%)) were used as reactants.

Typically, alcohol (0.25 mmol, except for 2,5-furandimethanol, 0.125 mmol), the catalyst (0.1 g), and DMF (10 mL) were loaded into the reactor. Then the reactor was filled with O_2 (0.5 MPa) as an oxidant for a certain period of time at stirring speed 500 rpm. It took approximately 14 min to reach the reaction temperature. At the end of the reaction, the reactor was immediately immersed in ice water, and subsequently, O_2 was released to terminate the reaction. For the selective oxidation of HMF, the reaction liquid sample was filtered and analyzed by high-performance liquid chromatography (HPLC) on a Shimadzu LC-20A instrument with a Shodex Sugar column and a refractive index detector. The mobile phase was a 0.5% H_2SO_4 aqueous solution. For the selective oxidation of the other alcohols, the liquid products were analyzed by gas chromatography on an Agilent 7890A with an HP-5 column and a flame ionization detector. The conversion of alcohols and the selectivity of the products were acquired on a carbon basis.

The Weisz–Prater criterion (C_{WP}) was calculated by to eliminate the mass transfer limitations according to the references [43,44] using the equation

$$C_{WP} = \frac{-r'_A \rho_c R^2}{D_e C_{AS}}, \quad (4)$$

where $-r'_A$ = reaction rate, kmol/kg-cat s; R = catalyst particle radius, m; ρ_c = solid catalyst density, kg/m³—here, ρ_c = 800 kg/m³; D_e = effective diffusivity coefficient, m²/s; C_{AS} = gas concentration of A at the catalyst surface, kmol A/m³.

The carbon balance of the reaction was obtained by using the known compounds for calibration. All the catalysts gave a carbon

balance above 97.0%. Because of the low loading and high dispersion of Fe, we measured the turnover frequency (TOF) on the total Fe metal atoms determined from by XRF, indicating the moles of HMF converted per Fe atom on the catalyst per hour (mol-HMF mol-Fe⁻¹h⁻¹, for short, h⁻¹). The HMF conversion for the TOF calculation in all case was below 10%. The carbon balance and TOF were calculated by the equations

$$\text{Carbon balance} = \frac{\text{Total moles of carbon in products}}{\text{Moles of carbon in substrate}}, \quad (5)$$

$$\text{TOF} = \frac{\text{Moles of HMF converted}}{\text{Fe atoms} \times \text{Time}}. \quad (6)$$

Because SCN⁻ can selectively bond with active Fe species and thus poison them [2,6,45,46], a KSCN titration experiment was performed to further quantify the active sites. The numbers of active sites were determined by the amounts of KSCN when the HMF conversion remained almost constant. Prior to the reaction, the catalyst (22 mg) and specified equivalent of KSCN solution (1.4 mg/mL) were mixed in the reaction. After 1 h stirring, HMF (25 mg) and O_2 (0.5 MPa) were added to the reaction system and heated to 100 °C in 14 min. Theoretically, the mole number of KSCN was considered as the content of active sites. The TOF were calculated based KSCN titration experiment by the equation

$$\text{TOF} = \frac{\text{Converted HMF molecules}}{\text{Active sites} \times \text{Time}}, \quad (7)$$

where the data of converted HMF molecules were calculated by multiplying the moles of HMF input with the HMF conversion difference with and without KSCN.

To determine the recyclability of MN_x/C-T, the used catalysts were recovered by centrifugation, washed, and dried overnight in an oven at 100 °C without further treatment. To evaluate the activities of the regenerated catalysts, the used catalysts were heat-treated under N_2 or NH_3/N_2 for 1 h.

3. Results and discussion

3.1. Structural properties of FeN_x/C-T

The textural properties and features of FeN_x/C-T were investigated using a battery of characterizations. The XRD patterns showed that the FeN_x/C-T catalysts from different pyrolysis temperatures had the same diffraction lines (Fig. S1 in the [Supplementary Data](#)). Only two peaks (24.8° and 43.7°) were observed, assigned to the diffraction of graphite from the carbon support [2,24]. There were no diffraction peaks attributed to Fe-containing crystalline phases, which indicated that no large particles existed in the FeN_x/C-T catalysts. The surface area and pore size distribution data of the FeN_x/C-T samples from N_2 adsorption–desorption measurements are listed in [Table S1](#). The specific surface area of the catalysts increased from 403 to 901 m²/g with the increase of pyrolysis temperature. The average pore size ranged from 4.2 to 5.1 nm with a feature of mesoporous materials. The Raman spectra indicated that the integrated intensity ratio of the D band at 1340 cm⁻¹ and the G band at 1590 cm⁻¹ (I_D/I_G) increased in the range 1.38–1.55 with increasing pyrolysis temperature (Fig. S2). This indicated that a higher pyrolysis temperature created more structural defects on the carbon supports [47,48].

To identify the dispersion states and morphologies of the Fe species in FeN_x/C-T, TEM and HAADF-STEM measurements were performed. In the bright-field images of FeN_x/C-900, no crystallized Fe species were observed (Fig. 1a, b, and S3), which were in good agreement with the results from the XRD pattern analyses. In the dark-field images of FeN_x/C-900, a few Fe species were identified

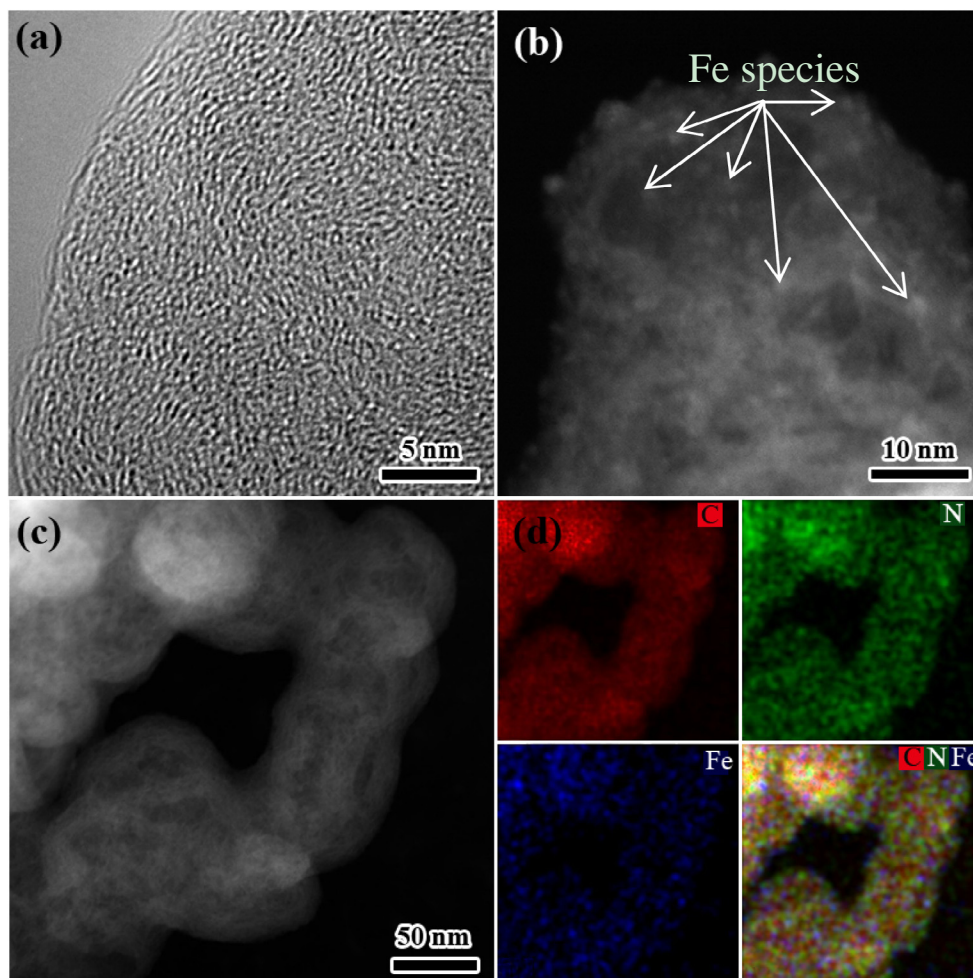


Fig. 1. TEM and HAADF-STEM images of $\text{FeN}_x/\text{C-900}$. (a) Bright-field image, (b, c) dark-field images, and (d) STEM mapping image.

(Fig. 1b). STEM mapping showed that the Fe species were integrated tightly with C and N (Fig. 1d).

There was a small difference in Fe content in the five catalysts, as indicated in Table 1: 1.31% for $\text{FeN}_x/\text{C-1000}$, 0.9% for $\text{FeN}_x/\text{C-900}$, 1.1% for $\text{FeN}_x/\text{C-800}$, 1.38% for $\text{FeN}_x/\text{C-700}$, and 0.89% for $\text{FeN}_x/\text{C-600}$. The N content of the catalysts depended critically on the pyrolysis temperature. Among them, the N content in the $\text{FeN}_x/\text{C-900}$ was 4.3%, which was higher than 2.7% for $\text{FeN}_x/\text{C-1000}$ and lower than 7.4% for $\text{FeN}_x/\text{C-800}$, 10.7% for $\text{FeN}_x/\text{C-700}$, and 14.4% for $\text{FeN}_x/\text{C-600}$.

3.2. Selective oxidation of alcohols over $\text{FeN}_x/\text{C-T}$ catalyst

We performed a series of experiments with the $\text{MN}_x/\text{C-900}$ catalysts for the selective oxidation of HMF. The results showed that only $\text{FeN}_x/\text{C-900}$ and $\text{CrN}_x/\text{C-900}$ could afford 100% and 88.6%

selectivity to DFF under the same reaction conditions; other $\text{MN}_x/\text{C-900}$ catalysts, such as $\text{CoN}_x/\text{C-900}$, $\text{CuN}_x/\text{C-900}$, and $\text{NiN}_x/\text{C-900}$, displayed lower activity or worse selectivity (Fig. S4). We then evaluated the influence of FeN_x catalysts with different carbon supports on the catalytic performance. These catalysts gave considerable HMF conversion, 51.6% for $\text{FeN}_x/\text{C-900}$, 61.4% for $\text{FeN}_x/\text{CNT-900}$, and 54.4% for $\text{FeN}_x/\text{XC72-900}$, with 100% selectivity to DFF over 1 h of reaction (Fig. S5). Based on the above experiments, we considered that the carbon support, regardless of its structure, was a quite good type of carrier for the FeN_x catalysts and that a specific metal center was needed for the selective oxidation of HMF. Therefore, we focus on the structure–performance correlation of $\text{FeN}_x/\text{C-T}$ catalysts in the following studies.

In the selective oxidation of HMF, all the $\text{FeN}_x/\text{C-T}$ catalysts exhibited 100% selectivity to DFF without the formation of FDCA with 0.5 MPa O_2 at 100 °C. However, the HMF conversion increased

Table 1
Elemental analyses of the $\text{FeN}_x/\text{C-T}$ catalysts obtained at different pyrolysis temperatures.

Catalyst	C/N	Content/wt. %			
		N ^a	C ^a	H ^a	Fe ^b
$\text{FeN}_x/\text{C-1000}$	34.0	2.7	91.8	0.9	1.31
$\text{FeN}_x/\text{C-900}$	20.3	4.3	87.3	1.7	0.90
$\text{FeN}_x/\text{C-800}$	11.1	7.4	82.5	1.6	1.10
$\text{FeN}_x/\text{C-700}$	7.2	10.7	77.1	1.9	1.38
$\text{FeN}_x/\text{C-600}$	5.5	14.4	78.9	2.2	0.89

^a Analyzed by element analysis.

^b Measured by XRF.

from 6.9% to 51.6% and then dropped to 34% as pyrolysis temperature increased from 600 to 1000 °C (Fig. 2). This finding indicated that the catalytic activity was not in line with the S_{BET} data of $\text{FeN}_x/\text{C-T}$ (Table S1). The TOF and reaction rate based on overall Fe atoms are summarized in Fig. 3 and Table S2. The reaction rates of $\text{FeN}_x/\text{C-900}$ and $\text{FeN}_x/\text{C-800}$ for HMF selective oxidation were similar (approximately $1.1\text{--}1.4 \times 10^{-3} \text{ mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$). The TOF values over $\text{FeN}_x/\text{C-900}$ and $\text{FeN}_x/\text{C-800}$ were 7.0 and 5.9 h^{-1} , respectively, which were 2–3 times higher than $\text{FeN}_x/\text{C-700}$ and $\text{FeN}_x/\text{C-1000}$. Because the Fe amount was almost the same in $\text{FeN}_x/\text{C-T}$ (Table 1), the variation of TOF should be caused by different numbers of active species. Unlike the results reported in the previous literature (Table S4) [8,26–28,30,31,33], the catalytic activity of $\text{FeN}_x/\text{C-900}$ was comparable to that of noble catalyst. Among a series of non-precious-metal catalysts, $\text{FeN}_x/\text{C-900}$ had higher TOF with lower ratio of metal to HMF (1/15) under relatively mild reaction conditions.

The TOF values based on KSCN titration experiments are summarized in Table S3 and Fig. S6. It can be seen that when KSCN was added into the system, the conversion of HMF decreased substantially; when the addition of KSCN was 0.2 equivalents of Fe content in the $\text{FeN}_x/\text{C-T}$, the conversion of HMF remained almost constant. According to the TOF definition (Eq. (7)), the numbers of active sites were 0.2 equivalents of Fe content. As for the 0.8 equivalents of Fe atoms left free in the poisoned catalysts, we assume that these Fe atoms were not the main contribution to the reaction [6]. Thus, the values of TOF-based KSCN titration experiments were higher than those for KSCN-free catalysts. The TOF values of $\text{FeN}_x/\text{C-900}$ and $\text{FeN}_x/\text{C-800}$ were 23.5 and 17.4 h^{-1} , respectively, which are approximately three times higher than the TOF based on overall Fe atoms (Table S2 and Fig. 3). The results indicate that $\text{FeN}_x/\text{C-900}$ and $\text{FeN}_x/\text{C-800}$ might have high concentration of active Fe species. The catalysts poisoned by KSCN also showed low conversion, indicating that the N-doped carbon could contribute to the oxidation and the activity was dependent on the pyrolysis temperature (Table S2). As for $\text{FeN}_x/\text{C-600}$, the contribution of N-doped carbon to the oxidation was approximately 60%, and that for $\text{FeN}_x/\text{C-700}$ and $\text{FeN}_x/\text{C-1000}$ was approximately 42% and 47%, respectively. In the case of $\text{FeN}_x/\text{C-900}$ and $\text{FeN}_x/\text{C-800}$, the contribution of N-doped carbon to the oxidation was approximately 32% and 38%, respectively.

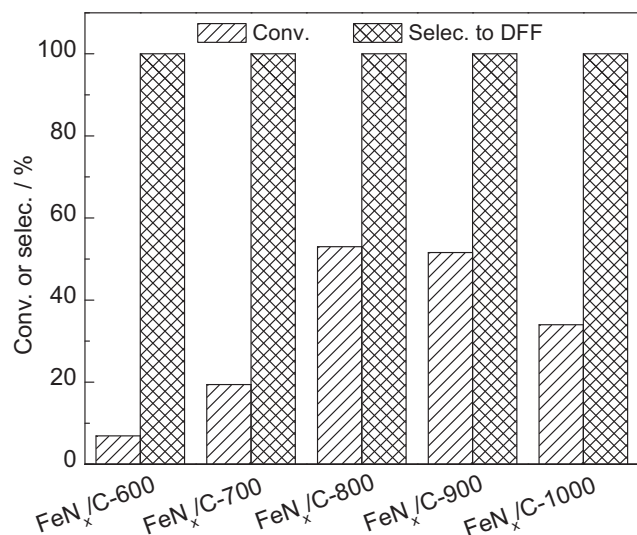


Fig. 2. HMF conversion and DFF selectivity on the $\text{FeN}_x/\text{C-T}$ catalysts at different pyrolysis temperatures. Reaction conditions: HMF 0.25 mmol, 32 mg; $\text{FeN}_x/\text{C-T}$ 0.1 g; DMF 10 mL; 100 °C; 1 h; 0.5 MPa O_2 .

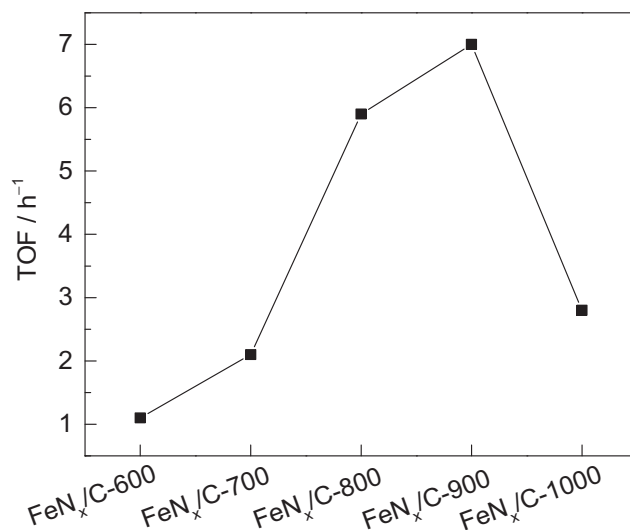


Fig. 3. The TOF values of HMF oxidation on the $\text{FeN}_x/\text{C-T}$ catalysts at different pyrolysis temperatures.

For $\text{FeN}_x/\text{C-900}$, we systematically investigated the time course for the product distribution of HMF oxidation. When the reaction time was prolonged to 5 h, the conversion of HMF reached 96.2%, and the selectivity to DFF decreased slightly from 100% to 98.9%, accompanying the formation of FDCA. When the reaction time was prolonged to 10 h, HMF was almost completely converted, and the selectivity to DFF dropped to 97.3% (Fig. 4). Through analysis of the time-course results, we found that $\text{FeN}_x/\text{C-900}$ could effectively restrain the excessive oxidation of DFF.

We further gained insight into the effects of the reaction time, stirring speed, reaction temperature, and catalyst amount on the activities of $\text{FeN}_x/\text{C-T}$ (Tables S5, S6, and S7). Based on the experimental data for $\text{FeN}_x/\text{C-800}$ and $\text{FeN}_x/\text{C-900}$, the yield of DFF exceeded 90% when the reaction time was prolonged. Taking the $\text{FeN}_x/\text{C-900}$ catalyst for an example, even with a reaction temperature reduced to 60 °C, the conversion of HMF reached 61.7% with a prolonged reaction time of 16 h. Meanwhile, the yield of DFF over $\text{FeN}_x/\text{C-900}$ increased from 28.5% to 51.6% after 1 h when the molar

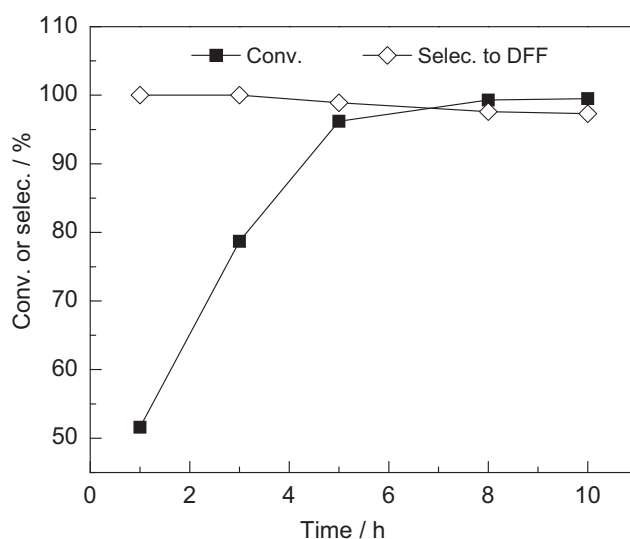


Fig. 4. HMF conversion and DFF selectivity on the $\text{FeN}_x/\text{C-900}$ catalyst as a function of reaction time. Reaction conditions: HMF, 0.25 mmol, 32 mg; $\text{FeN}_x/\text{C-900}$, 0.1 g; DMF, 10 mL; 100 °C; 0.5 MPa O_2 .

ratio of HMF to Fe was decreased from 30 to 15. Differently from FeN_x/C-800 and FeN_x/C-900, the HMF conversion over FeN_x/C-700 was only 48.2%, and the selectivity to DFF remained high (97.3%) after 8 h of reaction at 100 °C with 0.5 MPa O₂. The results indicated that a prolonged reaction time could not enhance the activity of FeN_x/C-700. Furthermore, we checked if there existed mass transfer limitations under present reaction conditions. The catalytic activity of FeN_x/C-900 remained constant when the stirring speed was increased from 300 to 800 rpm (Table S7). As for FeN_x/C-T catalysts, no large metal particles were observed by TEM and XRD; the size of particles were calculated as approximately 0.1 nm by TEM as shown in Fig. 1. Taking FeN_x/C-900 for an example, $C_{WP} = \frac{-r_A \rho_c R^2}{D_e C_{As}} = [3.1 \times 10^{-8} \text{ kmol/kg-cat s}] \times [8 \times 10^2 \text{ kg cat/m}^3] \times [5 \times 10^{-11} \text{ m}]^2 / [(2.9 \times 10^{-9} \text{ m}^2/\text{s}) \times [0.0052 \text{ kmol/m}^3]] = 1.6 \times 10^{-15} < 1$. The above results indicated there were no internal diffusion limitations under the present reaction conditions.

To further test the selective oxidation abilities of FeN_x/C-900, we chose several alcohols with typical structures as substrates. As shown in Table 2, FeN_x/C-900 exhibited extraordinary selective oxidation performance for various unsaturated monohydric alcohols containing β-H with above 97% selectivity to the corresponding aldehydes in high conversions (Table 2, entries 1–4). Dihydric alcohol was also smoothly transformed into the dialdehyde with 81.5% selectivity in 99.3% conversion (Table 2, entry 5). However, in the oxidation of cyclohexanol, only 16.6% conversion with 38.8% selectivity to cyclohexone was obtained after 10 h at 100 °C, accompanying some polymerization products of cyclohexanone and DMF based on the GC–MS analysis (Table 2, entry 6). For the selective oxidation of aliphatic alcohols, no products were detected on FeN_x/C-900 (Table 2, entries 7 and 8). It is important to note that a *p*–*π* conjugated bond existed in the unsaturated alcohols with aromatic conjugated structure. Compared with saturated alcohols, electron-withdrawing aromatic group may promote the activation and cleavage of hydroxymethyl C–H bonds to generate the corresponding product [8].

A series of control experiments have been carried out to understand the excellent performance of FeN_x/C-900 catalyst, as shown in Fig. S7. Under the same reaction conditions, the HMF conversion was 2.9% with 36.7% selectivity to DFF and 63.3% selectivity to FDCA on the Fe/C-900 catalyst. When the reaction was carried out on the CN_x-900 catalyst, the conversion of HMF was 11.3% with 93.4% selectivity to DFF and 6.6% selectivity to FDCA. There was no formation of DFF in the blank experiment. This proved that

N-doped carbon also contributes to the activity; notably, doped N was not the only way to promote the conversion and selectivity for this system. Considering that there are plentiful N-doped carbon species (*n*_N/*n*_{Fe} = 19:1) in FeN_x/C-900 catalyst, we can conclude that the Fe–N sites are more active than N-doped carbon sites.

3.3. Chemical state, active phase, and coordination environment of FeN_x/C-T

3.3.1. Chemical state and active phase of FeN_x/C-T

To further prove the active phase of FeN_x/C-T, based on the above experimental results, we measured the N1s XPS profiles of several FeN_x/C-T catalysts, as shown in Fig. 5. According to the results in the literature [10,49–52], the N1s data were deconvoluted into five peaks, which were categorized as cyano N (–CN), pyridinic N, Fe–N, pyrrolic N, and graphitic N, respectively. The curve fittings were performed by fixing the binding energy positions of corresponding N species with full width at half maximum as 1.4 eV for

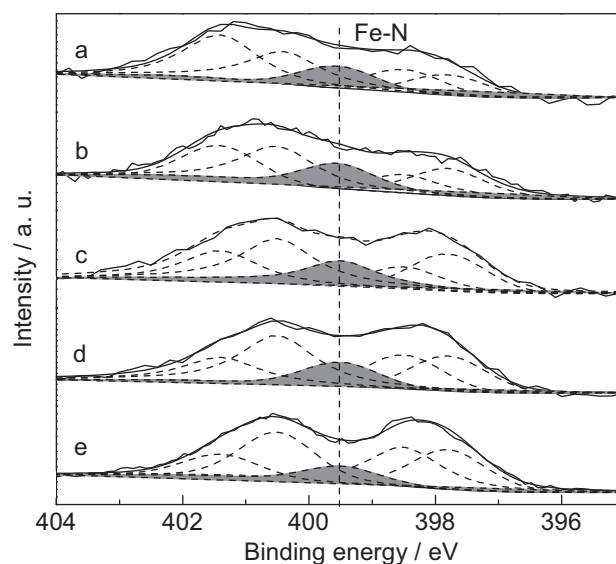


Fig. 5. N1s XPS profiles of the FeN_x/C-T catalysts. (a) FeN_x/C-900, (b) FeN_x/C-800, (c) FeN_x/C-1000, (d) FeN_x/C-700, and (e) FeN_x/C-600.

Table 2

Conversion and product distribution for the oxidation of different alcohols over FeN_x/C-900 catalysts.

Entry	Substrate	Product	Conv./mol. %	Selec./mol. %
1			100	98.6
2			100	100
3			99.5	97.3
4			63.9	100
5			99.3	81.5
6			16.6	38.8
7		–	0	0
8		–	0	0

Notes: Reaction conditions: substrate 0.25 mmol, except of 2,5-furandimethanol, 0.125 mmol; FeN_x/C-900 catalyst, 0.1 g; DMF, 10 mL. 100 °C, except benzyl alcohol, 80 °C; 10 h; 0.5 MPa O₂.

each peak (Table S8) [10,49–52]. The assignment and position and the corresponding content of these peaks are summarized in Tables S8, S9, and S10, respectively. The effective concentration of Fe–N species increased in the following order: $\text{FeN}_x/\text{C}-800 > \text{FeN}_x/\text{C}-900 > \text{FeN}_x/\text{C}-600 > \text{FeN}_x/\text{C}-700 > \text{FeN}_x/\text{C}-1000$. The $\text{FeN}_x/\text{C}-800$ and $\text{FeN}_x/\text{C}-900$ catalysts had the highest concentration of Fe–N, which is in line with their catalytic activity, as shown in Fig. 2. However, the $\text{FeN}_x/\text{C}-1000$ catalyst possessed the lowest concentration of Fe–N species, but it showed an activity higher than that of $\text{FeN}_x/\text{C}-700$ and -600.

To accurately prove whether Fe–N is an important active phase, we prepared another two catalysts, namely $\text{FeN}_x/\text{C}-700^*$ and $\text{FeN}_x/\text{C}-600^*$, to maintain a similar N content as $\text{FeN}_x/\text{C}-900$ (Table S11). In this case, the average N content in the bulk catalysts was similar but the concentrations of N-containing species were quite different under different pyrolysis temperature, which can exclude the effect of some unavailable N species and is beneficial for the investigation of active species. The catalytic results for the selective oxidation of HMF are listed in Fig. 6. In contrast to $\text{FeN}_x/\text{C}-900$, $\text{FeN}_x/\text{C}-600$, and $\text{FeN}_x/\text{C}-700$, the DFF selectivity decreased to 73.7% for $\text{FeN}_x/\text{C}-600^*$ and 68.2% for $\text{FeN}_x/\text{C}-700^*$ at 3.9% and 8.9% conversion of HMF, respectively. To probe the origins, XPS measurements were carried out. Fig. S8 illustrates the N1s XPS spectra of $\text{FeN}_x/\text{C}-900$, $\text{FeN}_x/\text{C}-600$, and $\text{FeN}_x/\text{C}-600^*$. The distribution of different N species is listed in Table S12. The concentration of Fe–N species was 16.9% in $\text{FeN}_x/\text{C}-900$ and decreased to 6.6% in $\text{FeN}_x/\text{C}-600^*$. Based on these results, we considered that the Fe–N species were the key to high catalytic activity and selectivity for the reaction. Furthermore, the N content might have an important influence on the catalytic performance.

On the other hand, the curve fittings of C1s and O1s XPS profiles are displayed in Fig. S9. The C1s XPS is deconvoluted to three peaks at 284.6, 285.4, and 286.1 eV in Fig. S9A, which were attributed to C–C, C=C, and C=N bonds of $\text{FeN}_x/\text{C}-T$, respectively [51,53,54]. The O1s XPS showed two peaks with bonding energies of 531.5 and 532.6 eV, respectively (Fig. S9B). The peak located at 531.5 eV correspond to C=O bonds, while that at 532.6 was attributed to C–OH [53–55]. The XPS results of C1s and O1s also indicated that there existed negligible Fe–C and Fe–O species.

3.3.2. Coordination environment of $\text{FeN}_x/\text{C}-T$

To further investigate the relationship between the performance and structure of $\text{FeN}_x/\text{C}-T$ catalysts, ESR measurements

were conducted to explore the states and coordination structures of Fe species. Fig. 7 displays the ESR spectra of the five $\text{FeN}_x/\text{C}-T$ catalysts. There were two signals at $g \sim 2.0$ and 4.3 over the entire magnetic field. The ESR signal at $g \sim 4.3$ originated from isolated Fe^{3+} species in tetrahedral and distorted tetrahedral coordination environments such as rhombic and tetragonal symmetry [56–60]. The Shelef and Vasiliev groups assigned the signal at $g \sim 2.0$ to ferri- species arising from the aggregate structure (dimer and trimer) [57,61,62].

For the five catalysts, an increase of pyrolysis temperature from 600 to 1000 °C is accompanied by intensity variations in the ESR signals at $g \sim 2.0$ and 4.3 regions. The intensity of the ESR signal at $g \sim 2.0$ decreased with increasing pyrolysis temperature, indicating that the agglomerated Fe species were unstable at high temperature [57]. However, the intensity of the ESR signal at $g \sim 4.3$ increased markedly when the pyrolysis temperature was raised from 600 to 700 °C, which indicates an increase of the tetrahedral coordinated Fe sites [57]. However, when the treatment temperature increased to 1000 °C, the intensity of the $g \sim 4.3$ signal in $\text{FeN}_x/\text{C}-1000$ was lower than in $\text{FeN}_x/\text{C}-900$. The results are consistent with the XPS analysis and prove that an excessively high temperature (1000 °C) can not promote the formation of active sites. To eliminate the influence of signal-to-noise ratio, plots of ESR intensity ratio of signals at $g \sim 4.3$ and 2.0 ($I_{4.3}/I_{2.0}$) versus pyrolysis temperature are shown in Fig. S10. It is found that the $I_{4.3}/I_{2.0}$ ratio increased rapidly with the increase of pyrolysis temperature from 600 to 900 °C. Although it is hard to quantify the concentrations of active species, it is clear that the signal at $g \sim 4.3$ increased and the signal at $g \sim 2.0$ decreased with increasing pyrolysis temperature. Additionally, the Fe content over all catalysts was almost the same, based on XRF, which suggested an increase in active species when the pyrolysis temperature was set at 600–900 °C. Based on these analysis results, we can conclude that the state of Fe species and the corresponding coordination structure of the $\text{FeN}_x/\text{C}-T$ catalyst are also very important factors in catalytic ability. The agglomerated Fe species have a negative effect on the catalytic activity and the isolated coordination Fe species may be the main active phase.

Taking the results of XPS and ESR into account, we assume that the catalytic activity not only is related to the concentration of Fe–N species but also depends on their chemical circumstances. The N content listed in Table 1 was the overall value of each catalyst. The amount distribution of Fe–N species in Table S9 was the

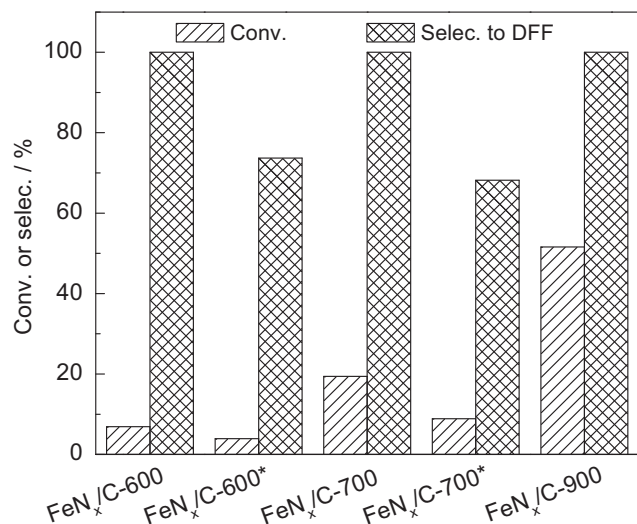


Fig. 6. HMF conversion on the $\text{FeN}_x/\text{C}-T$ catalysts with approximately equal N content. Reaction conditions: HMF, 0.25 mmol, 32 mg; catalyst, 0.1 g; DMF, 10 mL; 100 °C; 1 h; 0.5 MPa O_2 .

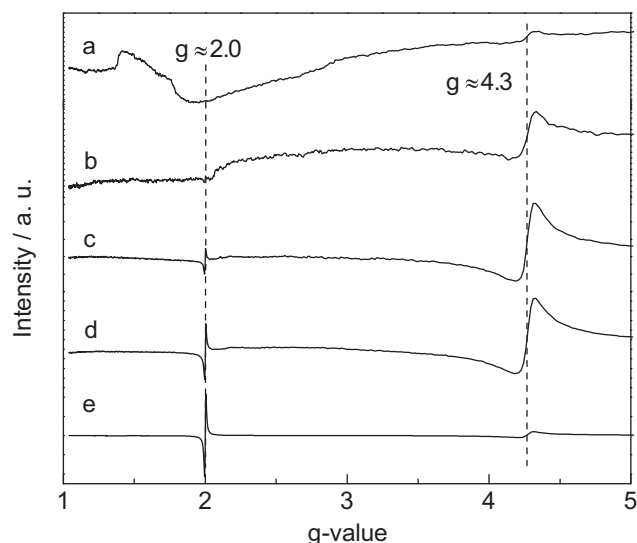


Fig. 7. ESR spectra of the $\text{FeN}_x/\text{C}-T$ catalysts with identical magnification and the same weight: (a) $\text{FeN}_x/\text{C}-1000$, (b) $\text{FeN}_x/\text{C}-900$, (c) $\text{FeN}_x/\text{C}-800$, (d) $\text{FeN}_x/\text{C}-700$, and (e) $\text{FeN}_x/\text{C}-600$ at -173 °C.

area percentage from N1s XPS. Thus, the surface concentration of Fe–N species was calculated by multiplying the amount of Fe–N species in Table S9 by the surface N concentration from XPS data. Table S10 shows the surface concentrations of N and Fe–N and the ratio of surface Fe–N to surface N. The FeN_x/C-800 and 900 had the highest concentrations of Fe–N and also the highest ratios of surface Fe–N to surface N, which were consistent with the catalytic activity. However, the FeN_x/C-1000 catalyst contained the lowest concentration of Fe–N species, but gave an activity higher than that of FeN_x/C-700 and FeN_x/C-600. One possible reason is that the redundant N covered or blocked the active Fe–N species in FeN_x/C-600, as evidenced by its having the lowest ratio of surface Fe–N to surface N. On the other hand, compared with the ESR signals of FeN_x/C-700 and FeN_x/C-600, FeN_x/C-1000 had almost no agglomeration of Fe species at $g \sim 2.0$. Meanwhile, the content of coordinated Fe species in FeN_x/C-1000 was less than in FeN_x/C-700 but more than in FeN_x/C-600 at $g \sim 4.3$, as depicted in Fig. 7. ESR results proved that the agglomerated Fe species had a negative effect on the catalytic activity and the isolated coordinated Fe–N species might be the main active site. Thus, it is easy to understand that the activity of FeN_x/C-1000 will be slightly higher than that of FeN_x/C-700 (Fig. 3 and Table S2).

To gain deep insight into the coordination environments and chemical states of the Fe species in the FeN_x/C-T catalysts, the four FeN_x/C-T samples were subjected to X-ray absorption fine structure (XAFS) spectroscopy. Fig. 8A shows the Fe K-edge XANES spectra of the four FeN_x/C-T samples. The pre-edge structures of the FeN_x/C-T samples were nearly the same, indicating the presence of an inversion center or octahedral structure. The Fe K-edge positions showed no considerable shifts among the four samples. The edge positions are shown in Fig. 8A, revealing a 2.0 eV shift with increasing treatment temperature, and the edge position is similar to that of Fe₂O₃ (7125.9 eV). Thus, Fe³⁺ species were predominant in FeN_x/C-900. Fig. 8B displays the Fourier transforms of the k^3 EXAFS spectra of the corresponding catalysts. The Fourier transformation was performed between 30 and 120 nm⁻¹ as depicted in Fig. S11. As shown in Fig. 8B, the first peak at 1.53 Å for FeN_x/C-800 and 900 corresponds to the Fe–N, Fe–C, and Fe–O bonds [63,64]. Because the results of C1s and O1s XPS exclude the existence of Fe–C and Fe–O, the first peak at 1.53 Å for FeN_x/C-800 and 900 corresponds to the Fe–N distance. The fitting results of the EXAFS are listed in Table S13. The EXAFS oscillations for the low-temperature-treated samples damped quickly, and the Debye–Waller factor became large. The coordination number for the first shell of FeN_x/C-800 and 900 was approximately 4.0 (3.9 ± 0.2 for FeN_x/C-800 and 3.8 ± 0.2 for FeN_x/C-900, respectively), indicating the formation of an Fe–N₄ species. The results are in accordance with the analysis of ESR and XPS. The second shell, appearing in FeN_x/C-800 and FeN_x/C-900 at 2.9 Å, can be assigned to the contribution of Fe–N–C [63]. Although a peak at 2.1 Å had the possibility of being Fe–Fe, the contribution was small and Fe nanoparticle formation might be negligible [64,65]. As for FeN_x/C-600 and FeN_x/C-700, their spectra showed a slightly different structure with much more disorder. Thus, it was difficult to determine the structure of FeN_x/C-600 and FeN_x/C-700 in detail. FeN_x/C-700 featured a mixture of the active phase appearing in FeN_x/C-900 and the precursor state of FeN_x/C-600, resulting in the EXAFS oscillations being reduced by the interference of the different structures. In summary, the EXAFS results proved that FeN_x/C-800 and 900 possessed Fe–N₄-like species.

3.4. Deactivation and regeneration of FeN_x/C-T

Attaining catalytic stability is always a great challenge for FeN_x/C-T catalysts [1,4,8,12,13]. More detailed studies are needed to focus on this aspect. Our study investigated the reasons behind

deactivation after the initial high catalytic performance and made an effort to effectively regenerate the catalyst structure and its performance.

The stability of the FeN_x/C-900 catalyst has been investigated carefully, and the results are summarized in Table S14 and Fig. 9. After the second recycling experiment without any treatment of FeN_x/C-900, the HMF conversion dropped to 23.4%, and only approximately a quarter of the initial activity of the first run was maintained. The selectivity to DFF also decreased from 99.1% to 84.4% (Table S14, entry 2). However, after heat treatment of used FeN_x/C-900 at 900 °C under N₂ for 1 h, the HMF conversion increased to 96.7% with 99.4% selectivity to DFF (Table S14, entry 3). Prolonging the heat treatment time to 3 h only increased the HMF conversion to 84.7%, and the DFF selectivity remained 99.4% (Table S14, entry 4). Fig. 9a shows the stability performance of the regenerated catalyst by calcination under N₂ for 1 h. The catalytic activity began to decrease again after three recycles. The yield of DFF decreased to 72.1% after six runs. However, we changed the regeneration atmosphere to 3% NH₃/N₂ after three runs. The yield of DFF was maintained at approximately 90% after six runs in Fig. 9b.

To further reveal the reasons behind the deactivation and regeneration, the used and regenerated FeN_x/C-900 catalyst was

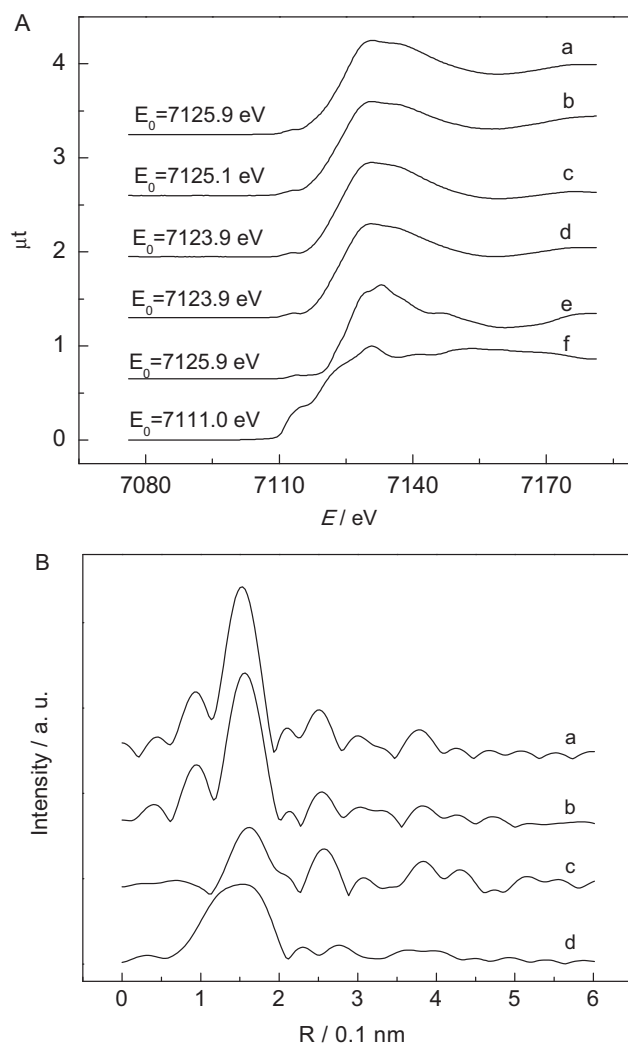


Fig. 8. (A) The normalized XANES profiles: (a) FeN_x/C-900, (b) FeN_x/C-800, (c) FeN_x/C-700, (d) FeN_x/C-600, (e) Fe₂O₃, and (f) Fe foil; and (B) the k^3 -weighted Fourier transform EXAFS profiles at the Fe K-edge of different samples: (a) FeN_x/C-900, (b) FeN_x/C-800, (c) FeN_x/C-700, and (d) FeN_x/C-600.

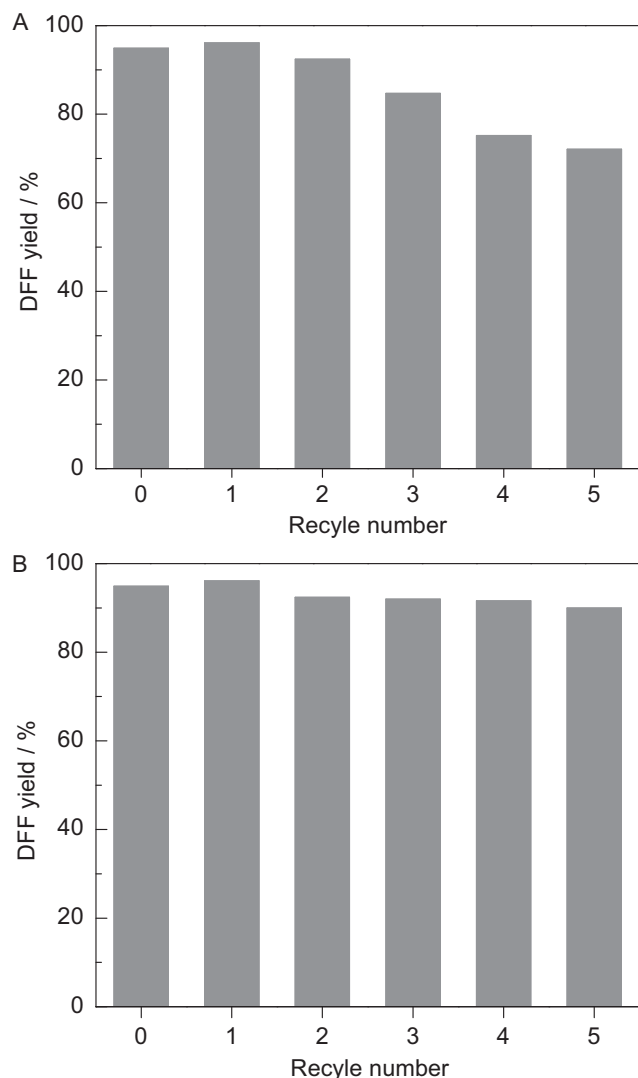


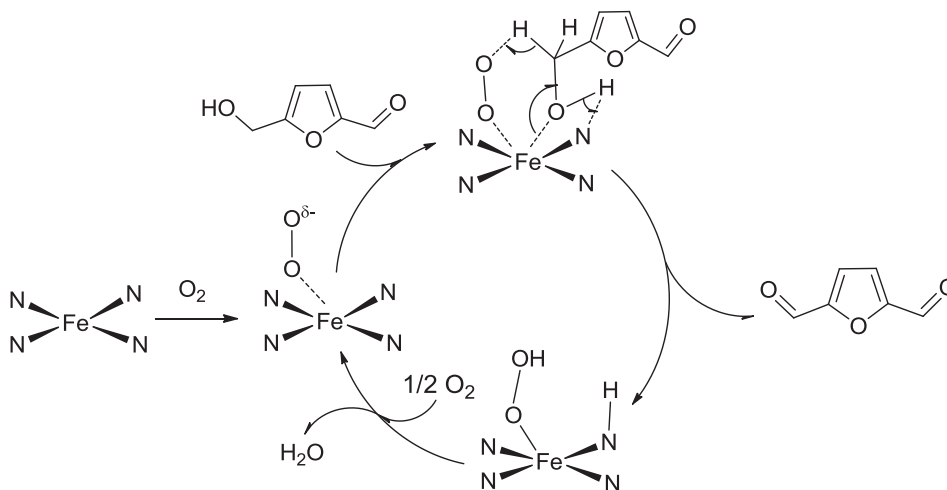
Fig. 9. Recycling results of the FeN_x/C-900 catalyst for the HMF oxidation. Reaction conditions: HMF, 0.25 mmol, 32 mg; FeN_x/C-900, 0.1 g; DMF, 10 mL; 100 °C; 5 h; 0.5 MPa O₂. (A) The FeN_x/C-900 catalyst was reused after calcination in N₂ at 900 °C for 1 h and (B) the FeN_x/C-900 catalyst was calcined in 3%NH₃/N₂ for 1 h at 900 °C after the third run and then reused.

characterized by N₂ adsorption-desorption measurement, elemental analysis, and ESR spectroscopy. Fig. S12 shows the ESR spectra of the FeN_x/C-900 catalyst under different conditions. For the used FeN_x/C-900 catalyst, an ESR signal at $g \sim 2.0$ appeared, suggesting the formation of aggregated Fe species. The decrease in ESR signal intensity at $g \sim 4.3$ indicated the loss of tetrahedrally coordinated Fe sites. Further, the drop in S_{BET} value after the reaction also suggested the occurrence of agglomeration (Table S15). For the regenerated FeN_x/C-900 catalyst, the ESR signal at $g \sim 2.0$ did not appear, and the intensity of the ESR line at $g \sim 4.3$ increased slightly. The results showed that the active Fe sites could regenerate in the heat treatment process without the formation of aggregated Fe species [57]. Thus, the agglomeration of Fe species and the loss of active Fe sites in the used FeN_x/C-900 catalyst were the main reasons for the catalyst's deactivation.

Table S16 lists the results of elemental analysis. After heat treatment, the N content of the FeN_x/C-900 catalyst was reduced. For the FeN_x/C-900 catalyst treated under N₂, the N content was only $\sim 1\%$ after six runs (Table S16, entry 4). For the FeN_x/C-900 catalyst treated under NH₃/N₂, the loss of N content was depressed. After six runs, the N content was maintained at $\sim 2\%$ (Table S16, entry 7). The supplement of N element might be an important method for effectively regenerating the Fe–N₄ structure and its performance.

3.5. Catalytic mechanism of FeN_x/C-T

In the selective oxidation of alcohols, the FeN_x/C-T catalysts exhibited high selectivity to the corresponding aldehydes, and the main active sites were Fe–N₄ species. The experimental results proved that the incorporation of N atoms suppressed the formation of FDCA and promoted the selectivity to the corresponding aldehyde (Fig. S6). Previous work has reported that doping with nitrogen groups offered coordinating sites for metal ions to generate the reactive phase for the reduction of O₂ [1,2,9,13,47]. Fe–N species could activate adsorbed molecular O₂ to create peroxy or superoxy oxygen species by donating electrons [2,9,10,66]. On the other hand, EXAFAS revealed that the coordination number of N to Fe atoms is approximately 4, indicating that the Fe species were likely in a structural configuration of unsaturated coordination. Meanwhile, it is also known that the Fe–N–C entity had high catalytic activity toward oxidation of H₂O₂ and heterocyclic compounds [2,6,67]. Hence, it is validated that the present FeN_x/C-T could exhibit catalytic activity in oxidation reactions [4,6]. When our work is combined with previous reports, a possible and plausible reaction



Scheme 1. The proposed catalytic pathway for the selective oxidation of HMF over FeN_x/C-T catalysts.

mechanism can be proposed to explain the selective oxidation of alcohols in Scheme 1.

In the reaction, molecular O_2 was adsorbed onto the Fe–N₄ active sites. It has been reported that the incorporation of N atoms enhanced the electronic density of the active sites [68]. Thus, an electron transferred from the Fe–N₄ active sites to adsorbed O_2 . After accepting the electron, the adsorbed O_2 became a peroxo species ($-O-O-$). After that, the proton H on the alcoholic hydroxyl group transferred to the N^{6-} species of the Fe–N₄ sites, and meanwhile, the O^{5-} of the hydroxy group interacted with the Fe^{5+} sites of the Fe–N₄ active phase. Then the β -H of the unsaturated alcohol transferred to the peroxo species to form H_2O , similarly to the ORR mechanism on FeN_x/C-T [10,66] and the corresponding aldehyde was released from the active sites.

4. Conclusions

In conclusion, a series of MN_x/C-T catalysts were prepared by a two-step pyrolysis method. Their catalytic performances in the selective oxidation of various alcohols were evaluated. The FeN_x/C-T catalysts obtained at different pyrolysis temperatures show promising selectivity to the corresponding aldehydes for the selective oxidation of unsaturated alcohols. In particular, the catalyst FeN_x/C-900 can perform selective oxidation of HMF to DFF with almost complete conversion and selectivity higher than 97% under the optimized conditions. A combination study including elemental analysis, XPS, ESR spectroscopy, EXAFS, and a KSCN titration experiment verifies that the main active site is Fe–N₄ in FeN_x/C-900 and for FeN_x/C-800, and the concentration of Fe–N₄ species and the chemical circumstances of Fe–N species are very important factors in the catalytic performance. The higher the Fe–N₄ concentration with more isolated Fe–N species, the higher the activity for the selective oxidation of HMF to DFF. As for the FeN_x/C-600 catalyst obtained at a low pyrolysis temperature, the active sites were largely attributed to the N-doped carbon species and the activity was quite low. A plausible reaction mechanism based on Fe–N₄ active sites is thus proposed. Moreover, we explain that the reason for catalyst deactivation is essentially the loss of effective Fe–N species by ESR measurements. The results demonstrate that the activity of FeN_x/C-900 catalysts can be regenerated by heat treatment under NH_3/N_2 . The present findings into the structures of FeN_x/C catalysts and their catalytic performance with molecular O_2 may shed new light on the design and understanding of such emerging transition-metal hydrides for various catalytic applications.

Acknowledgments

We acknowledge financial support from the National Key R&D Program of China (2017YFA0206801), the National Natural Science Foundation of China (91545115 and 21473145), the JST-CREST project “Innovative Catalysts” JPMJCR15P4, and the Program for Innovative Research Teams in Chinese Universities (IRT_14R31).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcat.2018.08.004>.

References

- [1] M. Lefèvre, E. Proietti, F. Jaouen, J.P. Dodelet, Iron-based catalysts with improved oxygen reduction activity in polymer electrolyte fuel cells, *Science* 324 (2009) 71–74.
- [2] Q. Wang, Z.Y. Zhou, Y.J. Lai, Y. You, J.G. Liu, X.L. Wu, E. Terefe, C. Chen, L. Song, M. Rauf, N. Tian, S.G. Sun, Phenylendiamine-based FeN(x)/C catalyst with high

- activity for oxygen reduction in acid medium and its active-site probing, *J. Am. Chem. Soc.* 136 (2014) 10882–10885.
- [3] K. Artyushkova, C. Walker, W. Patterson, P. Atanassov, Hierarchically structured non-PGM oxygen reduction electrocatalyst based on microemulsion-templated silica and pyrolyzed iron and cyanamide precursors, *Electrocatalysis* 5 (2014) 241–247.
- [4] D.H. Deng, X.Q. Chen, L. Yu, X. Wu, Q.F. Liu, Y.X. Liu, H. Yang, H.F. Tian, Y.F. Hu, P.P. Du, R. Si, J.H. Wang, X.J. Cui, H.B. Li, J.P. Xiao, T. Xu, J. Deng, F. Yang, P.N. Duchesne, P. Zhang, J.G. Zhou, L.T. Sun, J.Q. Li, X.L. Pan, X.H. Bao, A single iron site confined in a graphene matrix for the catalytic oxidation of benzene at room temperature, *Sci. Adv.* 1 (2015) e1500462.
- [5] M. Li, S.J. Wu, X.Y. Yang, J. Hu, L. Peng, L. Bai, Q.S. Huo, J.Q. Guan, Highly efficient single atom cobalt catalyst for selective oxidation of alcohols, *Appl. Catal. A* 543 (2017) 61–66.
- [6] W.G. Liu, L.L. Zhang, X. Liu, X.Y. Liu, X.F. Yang, S. Miao, W.T. Wang, A.Q. Wang, T. Zhang, Discriminating catalytically active FeN_x species of atomically dispersed Fe–N–C catalyst for selective oxidation of the C–H bond, *J. Am. Chem. Soc.* 139 (2017) 10790–10798.
- [7] L.L. Zhang, A.Q. Wang, W.T. Wang, Y.Q. Huang, X.Y. Liu, S. Miao, J.Y. Liu, T. Zhang, Co–N–C catalyst for C–C coupling reactions: on the catalytic performance and active sites, *ACS Catal.* 5 (2015) 6563–6572.
- [8] J.H. Xie, K.H. Yin, A. Serov, K. Artyushkova, H.N. Pham, X.H. Sang, R.R. Unocic, P. Atanassov, A.K. Datye, R.J. Davis, Selective aerobic oxidation of alcohols over atomically-dispersed non-precious metal catalysts, *ChemSusChem* 10 (2017) 359–362.
- [9] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt, *Science* 332 (2011) 443–447.
- [10] K. Artyushkova, A. Serov, S. Rojas-Carbonell, P. Atanassov, Chemistry of multitubular active sites for oxygen reduction reaction in transition metal–nitrogen–carbon electrocatalysts, *J. Phys. Chem. C* 119 (2015) 25917–25928.
- [11] C.H. Choi, W.S. Choi, O. Kasian, A.K. Mechler, M.T. Sougrati, S. Bruller, K. Strickland, Q. Jia, S. Mukerjee, K.J. Mayrhofer, F. Jaouen, Unraveling the nature of sites active toward hydrogen peroxide reduction in Fe–N–C catalysts, *Angew. Chem. Int. Ed.* 56 (2017) 1–5.
- [12] E. Proietti, F. Jaouen, M. Lefèvre, N. Larouche, J. Tian, J. Herranz, J.P. Dodelet, Iron-based cathode catalyst with enhanced power density in polymer electrolyte membrane fuel cells, *Nat. Commun.* 2 (2011) 1–9.
- [13] J. Liu, X.J. Sun, P. Song, Y.W. Zhang, W. Xing, W.L. Xu, High-performance oxygen reduction electrocatalysts based on cheap carbon black, nitrogen, and trace iron, *Adv. Mater.* 25 (2013) 6879–6883.
- [14] M. Hasan, M. Musawir, P.N. Davey, I.V. Kozhevnikov, Oxidation of primary alcohols to aldehydes with oxygen catalysed by tetra-n-propylammonium perruthenate, *J. Mol. Catal. A Chem.* 180 (2002) 77–84.
- [15] S. Mori, M. Takubo, K. Makida, T. Yanase, S. Aoyagi, T. Maegawa, Y. Monguchi, H. Sajiki, A simple and efficient oxidation of alcohols with ruthenium on carbon, *Chem. Commun.* 5159–5161 (2009).
- [16] W. Adam, F.G. Gelalcha, C.R. Saha-Moller, V.R. Stegmann, Chemoselective C–H oxidation of alcohols to carbonyl compounds with iodosobenzene catalyzed by (salen)chromium complex, *J. Org. Chem.* 65 (2000) 1915–1918.
- [17] T. Nishimura, T. Onoue, K. Ohe, S. Uemura, Palladium(II)-catalyzed oxidation of alcohols to aldehydes and ketones by molecular oxygen, *J. Org. Chem.* 64 (1999) 6750–6755.
- [18] G.T. Whiting, S.A. Kondrat, C. Hammond, N. Dimitratos, Q. He, D.J. Morgan, N.F. Dummer, J.K. Bartley, C.J. Kiely, S.H. Taylor, G.J. Hutchings, Methyl formate formation from methanol oxidation using supported gold–palladium nanoparticles, *ACS Catal.* 5 (2015) 637–644.
- [19] H. Wang, W. Fan, Y. He, J. Wang, J.N. Kondo, T. Tatsumi, Selective oxidation of alcohols to aldehydes/ketones over copper oxide-supported gold catalysts, *J. Catal.* 299 (2013) 10–19.
- [20] P.Y. Qi, S.S. Chen, J. Chen, J.W. Zheng, X.L. Zheng, Y.Z. Yuan, Catalysis and reactivation of ordered mesoporous carbon-supported gold nanoparticles for the base-free oxidation of glucose to gluconic acid, *ACS Catal.* 5 (2015) 2659–2670.
- [21] V.V. Costa, M. Estrada, Y. Demidova, I. Prosvirin, V. Kriventsov, R.F. Cotta, S. Fuentes, A. Simakov, E.V. Gusevskaya, Gold nanoparticles supported on magnesium oxide as catalysts for the aerobic oxidation of alcohols under alkali-free conditions, *J. Catal.* 292 (2012) 148–156.
- [22] A. Li, P. Zhang, X.X. Chang, W.T. Cai, T. Wang, J.L. Gong, Gold nanorod@TiO₂ yolk-shell nanostructures for visible-light-driven photocatalytic oxidation of benzyl alcohol, *Small* 11 (2015) 1892–1899.
- [23] J. Nie, J. Xie, H. Liu, Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on supported Ru catalysts, *J. Catal.* 301 (2013) 83–91.
- [24] S.S. Chen, P.Y. Qi, J. Chen, Y.Z. Yuan, Platinum nanoparticles supported on N-doped carbon nanotubes for the selective oxidation of glycerol to glyceric acid in a base-free aqueous solution, *RSC Adv.* 5 (2015) 31566–31574.
- [25] C.M. Zhou, W.P. Deng, X.Y. Wan, Q.H. Zhang, Y.H. Yang, Y. Wang, Functionalized carbon nanotubes for biomass conversion: the base-free aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over platinum supported on a carbon nanotube catalyst, *ChemCatChem* 7 (2015) 2853–2863.
- [26] J. Artz, S. Mallmann, R. Palkovits, Selective aerobic oxidation of HMF to 2,5-diformylfuran on covalent triazine frameworks-supported Ru catalysts, *ChemSusChem* 8 (2015) 672–679.
- [27] A. Takagaki, M. Takahashi, S. Nishimura, K. Ebitani, One-pot synthesis of 2,5-diformylfuran from carbohydrate derivatives by sulfonated resin and hydrotalcite-supported ruthenium catalysts, *ACS Catal.* 1 (2011) 1562–1565.

- [28] R.Q. Fang, R. Luque, Y.W. Li, Selective aerobic oxidation of biomass-derived HMF to 2,5-diformylfuran using a MOF-derived magnetic hollow Fe-Co nanocatalyst, *Green Chem.* 18 (2016) 3152–3157.
- [29] B. Liu, Z.H. Zhang, K. Lv, K.J. Deng, H.M. Duan, Efficient aerobic oxidation of biomass-derived 5-hydroxymethylfurfural to 2,5-diformylfuran catalyzed by magnetic nanoparticle supported manganese oxide, *Appl. Catal. A* 472 (2014) 64–71.
- [30] J.F. Nie, H.C. Liu, Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on manganese oxide catalysts, *J. Catal.* 316 (2014) 57–66.
- [31] H. Watanabe, S. Asano, S. Fujita, H. Yoshida, M. Arai, Nitrogen-doped, metal-free activated carbon catalysts for aerobic oxidation of alcohols, *ACS Catal.* 5 (2015) 2886–2894.
- [32] I. Sádaba, Y.Y. Gorbanev, S. Kegnaes, S.S.R. Putluru, R.W. Berg, A. Riisager, Catalytic performance of zeolite-supported vanadia in the aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran, *ChemCatChem* 5 (2013) 284–293.
- [33] N.T. Le, P. Lakshmanan, K. Cho, Y. Han, H. Kim, Selective oxidation of 5-hydroxymethyl-2-furfural into 2,5-diformylfuran over VO^{2+} and Cu^{2+} ions immobilized on sulfonated carbon catalysts, *Appl. Catal. A* 464–465 (2013) 305–312.
- [34] F. Neatu, R.S. Marin, M. Florea, N. Petrea, O.D. Pavel, V.I. Pârvulescu, Selective oxidation of 5-hydroxymethylfurfural over non-precious metal heterogeneous catalysts, *Appl. Catal. B* 180 (2016) 751–757.
- [35] L.N. Kong, W. Wei, Q.F. Zhao, J.Q. Wang, Y. Wan, Active coordinatively unsaturated manganese monoxide-containing mesoporous carbon catalyst in wet peroxide oxidation, *ACS Catal.* 2 (2012) 2577–2586.
- [36] T. Wang, Y.L. Meng, L.A. Zeng, J.L. Gong, Selective oxidation of methanol to dimethoxymethane over $\text{V}_2\text{O}_5/\text{TiO}_2\text{--Al}_2\text{O}_3$ catalysts, *Sci. Bull.* 60 (2015) 1009–1018.
- [37] Z.F. Yuan, W.N. Zhao, Z.P. Liu, B.Q. Xu, NaOH alone can be a homogeneous catalyst for selective aerobic oxidation of alcohols in water, *J. Catal.* 353 (2017) 37–43.
- [38] Y. Iwasawa, X-ray Absorption Fine Structure for Catalysts and Surfaces, World Scientific, Singapore, 1966.
- [39] T. Taguchi, REX2000 Version 2.5: improved DATA handling and enhanced user-interface, *AIP Conf. Proc.* (2006).
- [40] T. Taguchi, T. Ozawa, H. Yashiro, REX2000: yet another XAFS analysis package, *Phys. Scripta T* 115 (2005) 205–206.
- [41] J.J. Rehr, R. Albers, Theoretical approaches to x-ray absorption fine structure, *Rev. Mod. Phys.* 72 (2000) 621–654.
- [42] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Real space multiple scattering calculation of XANES, *Phys. Rev. B Condens. Matter Phys.* 58 (1998) 7565–7576.
- [43] P.B. Weisz, C.D. Prater, Interpretation of measurements in experimental catalysis, *Adv. Catal.* 6 (1954) 143–196.
- [44] S.T. Oyama, X.M. Zhang, J.Q. Lu, Y.F. Gu, T. Fujitani, Epoxidation of propylene with H_2 and O_2 in the explosive regime in a packed-bed catalytic membrane reactor, *J. Catal.* 257 (2008) 1–4.
- [45] X.D. Yang, Y. Zheng, J. Yang, W. Shi, J.H. Zhong, C. Zhang, X. Zhang, Y.H. Hong, X. Peng, Z.Y. Zhou, S.G. Sun, Modeling Fe/N/C catalysts in monolayer graphene, *ACS Catal.* 7 (2016) 139–145.
- [46] T.Y. Cheng, H. Yu, F. Peng, H.J. Wang, B.S. Zhang, D.S. Su, Identifying active sites of CoNC/CNT from pyrolysis of molecularly defined complexes for oxidative esterification and hydrogenation reactions, *Catal. Sci. Technol.* 6 (2016) 1007–1015.
- [47] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in graphene, *Phys. Rep.* 473 (2009) 51–87.
- [48] M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, L.G. Cancado, A. Jorio, R. Saito, Studying disorder in graphite-based systems by Raman spectroscopy, *Phys. Chem. Chem. Phys.* 9 (2007) 1276–1291.
- [49] D.H. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts, *Science* 351 (2016) 361–365.
- [50] K. Artyushkova, B. Kiefer, B. Halevi, A. Knop-Gericke, R. Schlögl, P. Atanassov, Density functional theory calculations of XPS binding energy shift for nitrogen-containing graphene-like structures, *Chem. Commun.* 49 (2013) 2539–2541.
- [51] R.T. Lv, T.X. Cui, M.S. Jun, Q. Zhang, A.Y. Cao, D.S. Su, Z.J. Zhang, S.H. Yoon, J. Miyawaki, I. Mochida, F.Y. Kang, Open-ended, N-doped carbon nanotube-graphene hybrid nanostructures as high-performance catalyst support, *Adv. Funct. Mater.* 21 (2011) 999–1006.
- [52] H.L. Peng, Z.Y. Mo, S.J. Liao, H.G. Liang, L.J. Yang, F. Luo, H.Y. Song, Y.L. Zhong, B. Q. Zhang, High performance Fe- and N- doped carbon catalyst with graphene structure for oxygen reduction, *Sci. Rep.* 3 (2013) 1–7.
- [53] O. Moradlou, Z. Rabiei, A. Banazadeh, J. Warzywoda, M. Zirak, Carbon quantum dots as nano-scaffolds for $\alpha\text{-Fe}_2\text{O}_3$ growth: preparation of $\text{Ti/CQD}/\alpha\text{-Fe}_2\text{O}_3$ photoanode for water splitting under visible light irradiation, *Appl. Catal. B Environ.* 227 (2018) 178–189.
- [54] E. Ech-chamikh, A. Essafi, Y. Ijdiyaou, M. Azizan, XPS study of amorphous carbon nitride (a-C:N) thin films deposited by reactive RF sputtering, *Sol. Energy Mater. Sol. C* 90 (2006) 1420–1423.
- [55] B. Lesiak, L. Kövér, J. Tóth, J. Zemek, P. Jiricek, A. Kromka, N. Rangam, $\text{C sp}^2/\text{sp}^3$ hybridizations in carbon nanomaterials—XPS and (X)AES study, *Appl. Surf. Sci.* 452 (2018) 223–231.
- [56] F. Gao, Y. Zheng, R.K. Kukkadapu, Y. Wang, E.D. Walter, B. Schwenzer, J. Szanyi, C.H.F. Peden, Iron loading effects in Fe/SSZ-13 NH_3 -SCR catalysts: nature of the Fe ions and structure–function relationships, *ACS Catal.* 6 (2016) 2939–2954.
- [57] A.V. Kucherov, M. Shelef, Quantitative determination of isolated Fe^{3+} cations in FeHZSM-5 catalysts by ESR, *J. Catal.* 195 (2000) 106–112.
- [58] M.S. Kumar, M. Schwidder, W. Grünert, A. Brückner, On the nature of different iron sites and their catalytic role in Fe-ZSM-5 DeNO_x catalysts: new insights by a combined EPR and UV/VIS spectroscopic approach, *J. Catal.* 227 (2004) 384–397.
- [59] U.I. Kramm, I. Herrmann-Geppert, J. Behrends, K. Lips, S. Fiechter, P. Bogdanoff, On an easy way to prepare metal-nitrogen doped carbon with exclusive presence of MeN_4 -type sites active for the ORR, *J. Am. Chem. Soc.* 138 (2016) 635–640.
- [60] A.N. Vasiliev, L.V. Shvanskaya, O.S. Volkova, A.V. Koshelev, E.A. Zvereva, G.V. Raganyan, I.A. Presniakov, A.V. Sobolev, A.M. Abakumov, Y.M. Lvov, Magnetism of natural composite of halloysite clay nanotubes $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and amorphous hematite Fe_2O_3 , *Mater. Charact.* 129 (2017) 179–185.
- [61] S.R. Pelluri, R. Singh, ESR and magnetization studies of $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3\text{--ZnO--PbO}$ glass system, *J. Magn. Magn. Mater.* 418 (2016) 206–212.
- [62] I. Ardelean, G. Salvan, M. Peteanu, V. Simon, C. Himcinschi, F. Ciorcas, EPR and magnetic susceptibility studies of $\text{B}_2\text{O}_3\text{--SrO--Fe}_2\text{O}_3$ glasses, *Mod. Phys. Lett. B* 13 (1999) 801–808.
- [63] U. Tylus, Q. Jia, K. Strickland, N. Ramaswamy, A. Serov, P. Atanassov, S. Mukerjee, Elucidating oxygen reduction active sites in pyrolyzed metal-nitrogen coordinated non-precious-metal electrocatalyst systems, *J. Phys. Chem. C* 118 (2014) 8999–9008.
- [64] C. Domínguez, F.J. Pérez-Alonso, M.A. Salam, S.A. Al-Thabaiti, M.A. Peña, F.J. García-García, L. Barrio, S. Rojas, Repercussion of the carbon matrix for the activity and stability of Fe/N/C electrocatalysts for the oxygen reduction reaction, *Appl. Catal. B* 183 (2016) 185–196.
- [65] U.I. Kramm, J. Herranz, N. Larouche, T.M. Arruda, M. Lefevre, F. Jaouen, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, S. Mukerjee, J.P. Dodelet, Structure of the catalytic sites in Fe/N/C-catalysts for O_2 -reduction in PEM fuel cells, *Phys. Chem. Chem. Phys.* 14 (2012) 11673–11688.
- [66] N. Ramaswamy, U. Tylus, Q. Jia, S. Mukerjee, Activity descriptor identification for oxygen reduction on nonprecious electrocatalysts: linking surface science to coordination chemistry, *J. Am. Chem. Soc.* 135 (2013) 15443–15449.
- [67] X. ui, Y. Li, S. Bachmann, M. Scalone, A.E. Surkus, K. Junge, C. Topf, M. Beller, Synthesis and characterization of iron-nitrogen-doped graphene/core-shell catalysts: efficient oxidative dehydrogenation of N-heterocycles, *J. Am. Chem. Soc.* 137 (2015) 10652–10658.
- [68] V.V. Strelko, V.S. Kuts, P.A. Thrower, On the mechanism of possible influence of heteroatoms of nitrogen, boron and phosphorus in a carbon matrix on the catalytic activity of carbons in electron transfer reactions, *Carbon* 38 (2000) 1499–1503.