Green Chemistry



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Cite this: DOI: 10.1039/c9gc01674k

An active, selective, and stable manganese oxide-supported atomic Pd catalyst for aerobic oxidation of 5-hydroxymethylfurfural[†]

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Here we report for the first time a Pd-MnO₂ catalyst with a single-atom feature that can convert 5-hydroxylmethyfurfural (HMF) into the important bioplastic building block 2,5-furandicarboxylic acid (FDCA) with a high yield of 88% in aqueous solution using O₂ as an oxidant at ambient pressure. Pd-MnO₂ shows higher activity in the productivity of FDCA (100.91 mmol h⁻¹ g_{Pd}^{-1}) than its Pd nanoparticle counterpart (45.57 mmol h⁻¹ g_{Pd}^{-1}) and state-of-the-art Pd-based catalysts. Pd-MnO₂ displays promising recyclability with no degradation after five catalytic runs. Experimental and theoretical results suggest that the singleatom Pd sites that have enhanced binding affinity to HMF and their surrounding sites on the MnO₂ support work synergistically toward HMF oxidation.

1. Introduction

Received 20th May 2019,

DOI: 10.1039/c9gc01674k

Accepted 5th July 2019

rsc.li/greenchem

Sustainable conversion of renewable biomass, such as lignocellulose and rotten grains, into various high value-added products has attracted significant attention as a promising substitute for non-renewable resources for the manufacture of key building-block chemicals.¹⁻⁸ 5-Hydroxymethyfurfural (HMF), as an ideal platform compound derived from cellulose or cellulose-derived carbohydrates, can be used for the synthesis of various chemical products.^{2,9–11} 2,5-Furandicarboxylic acid (FDCA) obtained from oxidation of HMF is an important inter-

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^gRIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan ^hInternational Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan mediate in the production of environmentally friendly biobased plastics (*e.g.* polyethylene furanoate).¹¹⁻¹³

Oxidation of HMF can produce several furan chemicals, for example, 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), and FDCA. Substantial progress has been made in converting HMF to FDCA using O2 as an oxidant and catalyzed by supported metal nanoparticle catalysts, such as Pt,12,14-17 Pd,^{4,11,13,18-20} Au,^{5,21-24} Ru²⁵⁻²⁸ and their bimetallics,²⁹⁻³² in an aqueous medium. To obtain a superior yield of FDCA, earlier researchers mostly focused on the composition and dispersion of noble metals and reaction parameters, such as elevated pressures, temperatures, and properties and dosages of the base, to assist in oxidation of the hydroxyl group of HMF. Very recently, the properties of catalysts, such as acid-alkali catalysts derived from functionalized carbon5,12,15,16,33 or doped hydroxide supports,^{4,22,24,31} have been investigated in order to replace the homogeneous alkali-catalyzed aerobic oxidation of HMF in water. However, high oxygen pressure (up to 2.4 MPa) is usually required to achieve good yields of FDCA in these reaction systems. For example, Kim et al. reported that MnCo₂O₄ spinel-supported ruthenium catalysts showed high catalytic activity for oxidation of HMF to FDCA, with a high yield of 99.1% at 120 °C for 10 h under 2.4 MPa air pressure, but low FDCA productivity (33 mmol h⁻¹ g_{Ru}⁻¹).³⁴ In addition, if metal nanoparticles (NPs) interacted weakly with the support, aggregation or leaching of NPs often occurred and resulted in low catalytic recyclability for this reactions.^{16,17} Acknowledging these important achievements, there is still a need to search for high FDCA productivity under milder con-

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[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ c9gc01674k

ditions for the oxidation of HMF to FDCA, and for recycling of catalysts for repeated use.

Single-atom catalysts (SACs), viewed as a new frontier in catalysis, have attracted increasing attention.^{35–41} Downsizing metal nanoparticles into single atoms not only improves the atomic efficiency, but also gives rise to new and intriguing catalytic properties owing to the quantum size effect and enhanced electronic metal–support interactions.⁴² Recent reports have shown that SACs exhibit outstanding catalytic performances in thermocatalysis (*e.g.* CO oxidation,⁴³ water gas shift,⁴⁴ hydrogenation of alkynes⁴⁵), electrocatalysis (*e.g.* oxygen reduction reaction,⁴⁶ oxygen evolution reaction⁴⁷), and photocatalysis.⁴⁸ Despite these significant advances, the application of SACs in oxidation of HMF is rare. It is both technologically and fundamentally important to make a comparative study of SACs and their NP counterparts for HMF oxidation, and to probe the underlying mechanism.

To construct an ideal catalyst for HMF oxidation, we incorporated atomic Pd into the crystalline lattice of a metal oxide support, thereby creating maximized interfacial sites and inducing favorable electronic metal–support interactions for activating HMF. A reducible oxide with rich oxygen vacancies that can effectively activate molecular oxygen is generally used as a support. Comparing the commonly reported reducible oxide supports (*e.g.* CeO₂,^{38,49,50} CoO_x,⁵¹ and NiO⁵²), MnO_x-based materials have attracted growing interest due to their eco-friendly and noncarcinogenic characteristics. Recent results indicate that MnO_x possesses moderate activity for the oxidation of HMF into FDCA.^{53–58} However, the reaction usually requires a pressurized system (0.8–2.0 MPa) with a long reaction period (\geq 12 h).

Here, we selected MnO₂ as the support. Synergistic interaction between atomic Pd and the surrounding sites of the MnO₂ support is expected to enhance the catalytic performance for HMF oxidation. Supported atomic Pd on MnO₂ was found to be more active, more selective and more stable than its nanoparticle counterpart. Extensive characterizations, including X-ray photoelectron spectroscopy (XPS), aberration-corrected high-angle annual dark-field scanning transmission electron microscopy (HAADF-STEM), and X-ray adsorption spectroscopy (XAS), were applied to probe the atomic structure and physicochemical properties of these catalysts. Quantum chemistry calculations were conducted to understand the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

The Pd-MnO₂ catalyst was prepared by mixing MnSO₄·H₂O, $(NH_4)_2S_2O_8$, Pd(NO₃)₂·2H₂O and $(NH_4)_2SO_4$ in an aqueous solution. The solution was then transferred into a Teflon-lined stainless steel autoclave and heated at 140 °C for 12 h, and, finally, allowed to cool down to room temperature. The black precipitate was collected, filtered, washed several times with water and dried at 120 °C for 12 h. The undoped α -MnO₂ nanowire was prepared under identical conditions except with the addition of Pd(NO₃)₂·2H₂O. The Pd nanoparticle deposited on

MnO₂ (denoted as PdNP/MnO₂) was prepared using the following procedure: 20 mg polyvinylpyrrolidone (PVP) was added into Pd(NO₃)₂ solution under stirring for 30 min. The α -MnO₂ nanowire was added into the above solution with stirring for another 30 min. Finally, NaBH₄ solution was dropped slowly into the mixture. After stirring for 30 min, the black powder obtained was filtered, washed until pH = 7 and dried in the oven at 120 °C for 12 h.

2.2. Characterization

Synchrotron X-ray diffraction (SXRD) measurements were performed at the beamline BL44B2 of SPring-8 (Hyogo, Japan). The Pd-MnO₂ sample was sealed in borosilicate glass capillaries under vacuum and data collected using a Debye-Scherrer camera with an imaging plate installed as an X-ray detector. The incident wavelength was 0.5003 Å. Calibration was achieved by applying CeO₂ as the standard. High-resolution transmission electron microscopy (HRTEM) was performed using the FEI Tecnai G2, to investigate the microstructure. Sub-Ångström-resolution HAADF-STEM images were recorded on a JEOL ARM200F equipped with a CEOS probe corrector and with a guaranteed resolution of 0.08 nm. XPS was performed on a Thermo Scientific K-Alpha XPS 33 spectrometer using an Al-Ka X-ray source (1486.6 eV). The C 1s photoelectron line was used for spectral calibration using the reference position with a binding energy (C 1s) of 284.8 eV.

XAS measurements were carried out at the BL14W1 station of the Shanghai Synchrotron Radiation Facility (SSRF, 3.5 GeV, 250 mA in maximum, Si (311) double crystals).⁵⁹ XAS spectra were recorded in fluorescence mode. IFEFFIT software packages were applied to analyze the data. The extended X-ray absorption fine structure (EXAFS) contributions were separated from different coordination shells using a Hanning window $(dk = 1.0 \text{ Å}^{-1})$. The quantitative curve fittings were performed in *R*-space (1.0–3.2 Å) with a Fourier transform *k*-space range of 3.0-12.0 Å⁻¹ employing the ARTEMIS module of IFEFFIT. All fits were performed in R-space with a k-weight of 2. The overall amplitude reduction factor, S_0^2 , was fixed at the best-fit value of 0.73, which was determined from fitting the data for metal Pd foil. The EXAFS R-factor for measurement of the percentage misfit of the theory to the data was used to evaluate the goodness-of-fit. Specifically, the R-factor is defined as:

$$R = \frac{\sum_{i=1}^{N} (\text{data}_i - \text{fit}_i)^2}{\sum_{i=1}^{N} (\text{data}_i^2)}$$

All raw data in *k*-space weighted by 0 were extracted from Athena software, and during wavelet transform (WT) analysis the data were weighted by 2.

 H_2 -Temperature programmed reduction (H_2 -TPR) and O_2 temperature programmed desorption (O_2 -TPD) were carried out on an AutoChem II 2920 adsorption apparatus equipped with a thermal conductivity detector (TCD). Typically, for H_2 -TPR, 40 mg of sample was loaded and pretreated under He with a flow of 50 mL min⁻¹ at 150 °C for 1 h. After cooling, the gas was changed to 10% H_2/Ar with a flow of 50 mL min⁻¹ and, meanwhile, the temperature was programmed to increase to 400 °C at a rate of 10 °C min⁻¹. For O₂-TPD, about 40 mg of sample was pretreated by flowing gas of 20% O₂/He at 100 °C for 2 h. Then, after cooling to 50 °C, the temperature was elevated to 700 °C at a rate of 10 mL min⁻¹ in He.

2.3. Catalytic tests

HMF oxidation was performed in a three-mouth bottle under atmospheric pressure, with a flow rate of 25 mL min⁻¹ 10% O₂ in Ar. Typically, 100 mg of catalyst was suspended in 100 ml of deionized water containing 0.6 mmol HMF and 2.4 mmol K₂CO₃. Then, the reactor was heated to 100 °C under vigorous stirring (900 rpm). Samples of the reaction mixture were withdrawn, filtered with 0.2 µm PTFE filters and analyzed using high-performance liquid chromatography on a Shimadzu LC-16 equipped with a UV detector and a C18 chromatographic column. A mixture of acetonitrile and a 0.1 wt% aqueous acetic acid solution, with a volume ratio of 10/90, was used as the mobile phase, and the flow rate was 1 ml min⁻¹. Products were characterized using the external standard method. The HMF conversion rate was defined as the molar percentage of HMF converted in the reaction, while the selectivity of each product was defined as the molar percentage of each product in the converted HMF.

2.4. DFT calculations

All spin-polarized calculations were carried out using the Vienna ab initio simulation package version 5.3.3, which is a plane wave density functional code. The electron-electron exchange and correlation interactions were described using the generalized gradient approximation with the form of the Perdew-Burke-Ernzerhof function. The projector-augmented wave method was employed to describe the interaction between the core and the valence electrons. The wave functions were expanded in plane wave basis sets with a cutoff energy of 400 eV. The convergence criteria for the electronic self-consistent iteration and the ionic relaxation loop were set to values of 1 \times 10 $^{-5}$ eV and 1 \times 10 $^{-4}$ eV Å $^{-1},$ respectively. Brillouin zone integration was performed with k-point sampling using a Monkhorst-Pack (MP) grid of 3 × 3 × 1 and $5 \times 5 \times 1$ for bulk and slab models, respectively, to ensure that the calculations can be done in a reasonable time. The Methfessel-Paxton method was used to determine the valence electron occupancies, with a smearing width of 0.1 eV.

The slab models of Pd-MnO₂ and Pd₁₃/MnO₂ surfaces were constructed with 3×2 surface unit cells. The bottom Mn layer and two O layers were fixed, while the rest of the atoms were fully relaxed. The adsorption energy (E_{ads}) and O vacuum-forming energy (E_{vacu}) were defined according to the following equations:

 $E_{
m ads} = E_{
m HMF}$ -slab $- E_{
m slab} - E_{
m free \ HMF}$ $E_{
m vacu} = E_{(-{
m O})}$ -slab $+ 1/2E_{
m free \ O_2} - E_{
m slab}$

where $E_{HMF-slab}$ is the total energy for HMF adsorption structures, E_{slab} is the total energy for the Pd/MnO₂ slab structure, $E_{(-O)-\text{slab}}$ is the total energy of the Pd-MnO₂ slab losing one oxygen atom, and $E_{\text{free HMF}}$ and $E_{\text{free O}_2}$ are the energies of free HMF and free O₂ in vacuum.

3. Results and discussion

3.1. Structure characterization of Pd-MnO₂ and PdNP/MnO₂

MnO₂-supported atomic Pd catalyst (denoted as Pd-MnO₂) was synthesized via hydrothermal treatment of a mixed aqueous solution of Pd(NO₃)₂, MnSO₄, (NH₄)₂SO₄, and (NH₄)₂S₂O₈ at 140 °C for 12 h. Pd²⁺ ions were expected to dope into the crystalline framework of the oxide support during the crystallization growth of MnO₂. Fig. 1(a and b) shows the typical TEM image. The as-prepared Pd-MnO₂ shared identical nanowire morphology with undoped α-MnO₂ (Fig. S1[†]). The average diameter of the Pd-MnO₂ nanowire was approximately 10 nm. Energy dispersive spectroscopy (EDS) mapping confirmed the co-existence of Pd, O and Mn (Fig. 1(d-f)). No Pd aggregates were detected from Pd signals (Fig. 1(f)), suggesting that the Pd was uniformly distributed throughout the nanowire structure. The HAADF-STEM images, with a guaranteed resolution of 0.08 nm, show the presence of bright dots, which correspond to Pd single atoms (Fig. 1(g and h)). The actual Pd loading of Pd-MnO2 was determined to be 1.31 wt% by inductively coupled plasma optical emission spectrometry (ICP-OES).



Fig. 1 (a, b) TEM and (c-f) HAADF-STEM images of Pd-MnO₂. (d-f) EDS elemental mapping images showing the distribution of Mn, O, and Pd, respectively. (g) Sub-Ångström-resolution HAADF-STEM image, Pd single atoms are highlighted by red circles. (h) Intensity profile of the scan along the dashed frame marked in (g).

The contrast sample PdNP/MnO₂ was prepared using a conventional deposition precipitation method. TEM characterization (Fig. 2(a–c)) showed the presence of tiny Pd NPs with an average size of ~2 nm that were firmly attached to the MnO₂ surface. The HRTEM image shows clear lattice fringes with interspacing of 0.22 nm (Fig. 2(c)), corresponding to the (111) plane of metallic Pd. EDS mapping shows the intensified Pd signal from the Pd NPs (Fig. 2(d–g)). The Pd loading measured by ICP-OES was found to be 2.23 wt%.

Previous research has stated that for reducible oxide-supported SACs the metal single atoms may locate at several different types of site in the crystalline support, including being adsorbed onto the surface,^{43,44,60,61} embedded in the crystalline lattice or decorated at crystalline defects.38,62-65 To determine the bonding environment of Pd-MnO₂ accurately, we carried out SXRD and XAS measurements. Fig. 3(a) shows the SXRD pattern of Pd-MnO2 and its fitted line. The Pd-MnO2 sample shows increased lattice parameters of a = b = 9.895 Å, c = 2.857 Å, and V = 279.735 Å³, compared with a = b = 9.881 Å, c = 2.855 Å, and V = 278.710 Å³ for undoped α -MnO₂, as determined by the Riveted refinement. This result suggests that Pd atoms with large ionic radii may substitute Mn sites in MnO₂. Such lattice doping of low valent ions usually leads to the creation of oxygen vacancies to maintain charge neutrality, as has been frequently reported in reducible oxide-supported catalysts. 38,49,63,64,66

Fig. 3(b and c) shows the X-ray absorption near-edge spectroscopy (XANES) and EXAFS spectra. The Pd K-edge absorption of Pd-MnO₂ is close to that of PdO, which indicates that the Pd valence is around +2. Fourier transformation (FT) of EXAFS was conducted. The FT-EXAFS curve of Pd-MnO₂ shows a prominent peak at ~1.5 Å, which is in line with the Pd–O coordination of PdO (Fig. 3(c)). Quantitative FT-EXAFS fitting (Fig. S2 and Table S1†) yields an average Pd–O bond length of $d_{Pd-O-1} \sim 2.0$ Å, and a coordination number (CN) of 4.5 in the



Fig. 2 (a, b) TEM, (c) HRTEM and (d-g) HAADF-STEM images of PdNP/ MnO_2 . (e-g) Elemental mapping showing the distribution of Mn, O, and Pd, respectively.



Fig. 3 XANES and EXAFS analysis: (a) SXRD data and refinement of Pd-MnO₂. (b) The normalized XANES spectra at the Pd K-edge of Pd foil, PdO, and Pd-MnO₂. (c) The k^3 -weighted FT-EXAFS spectra of the Pd K_{III}-edge without phase-shift correction. (d) WT contour plots of Pd-MnO₂ and MnO₂. Note: The WT plot of Pd-MnO₂ was separated into two figures. Two peaks located in the range 2–4 Å were intentionally enhanced for better comparison. The full WT plot is provided in Fig. S3.†

first nearest neighbor coordination shell. Two weak shoulder peaks centered at 2.4 Å and 2.9 Å were also observed, which can be attributed to overlapping contributions from Pd clusters and high shell Pd–Mn coordination, respectively. The CN of Pd–Pd was estimated to be 1.5, suggesting the presence of a small amount of Pd clusters. Wavelet transformation of EXAFS was further applied to distinguish back-scattering atoms. Fig. 3(d) shows the WT plot of Pd-MnO₂ with improved resolution in *R*-space using Morlet parameters of $\kappa = 25$ and $\eta = 1$. The WT contour plot of Pd-MnO₂ is similar to that of undoped MnO₂ (Fig. 3(e)), which suggests that Pd species in Pd-MnO₂ predominantly exist as single atoms and substitute Mn sites in the crystalline lattice.

3.2. Catalytic performance

 α -MnO₂ nanowire.supported, atomically dispersed and nanosized Pd species were evaluated in the aerobic oxidation of HMF under mild reaction conditions (aqueous media under ambient pressure). The profiles of reaction rate *versus* reaction time are shown in Fig. 4 and the main product was FDCA. Other side products were DFF, HMFCA and FFCA. The conver-

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Fig. 4 Catalytic performance and stabilities of the Pd-MnO₂ (a, b) and PdNP/MnO₂ catalysts (c, d). Reaction conditions: m(HMF)/m(catalyst) = 0.8, $n(HMF) : n(K_2CO_3) = 1 : 4$, water as solvent with an O₂ flow rate of 25 mL min⁻¹, T = 100 °C, 0.1 MPa.

sion rates of HMF over both Pd-MnO2 and PdNP/MnO2 samples increased with the reaction time. As the reaction exceeded 4 h, HMF was completely converted into FDCA, with 88.1% and 67.8% yields for Pd-MnO₂ and PdNP/MnO₂, respectively (Table 1). Fig. 4(a) shows that the Pd-MnO₂ sample has an FDCA production rate of 50.80 mmol mmol_{Pd}⁻¹, which is much higher than that of PdNP/MnO2 (18.01 mmol $mmol_{Pd}^{-1}$). Meanwhile, from Table 1 it can be seen that Pd-MnO₂ gives 100.91 mmol $h^{-1} g_{Pd}^{-1}$ of FDCA productivity, which is higher than that for nanosized Pd species (45.57 mmol h^{-1} g_{Pd}^{-1}). Comparing the activity of the Pd-MnO₂ and PdNP/MnO₂ catalysts by normalizing per exposed Pd atom, Pd-MnO₂ is still more active in the production of FDCA (Table S3[†]). In Table 1, the catalytic performance of Pd-MnO₂ is compared with commercially available Pd/C catalyst and recently reported Pd nanoparticle-based catalysts. Although the reported 4%Ru/MnO₂ catalyst has a high FDCA yield (99.1%), high O₂ pressure (2.4 MPa) was required.

Of the catalysts shown, Pd-MnO₂ shows an exceptionally high FDCA productivity under mild conditions.

The influence of catalyst loading and HMF dosage on HMF oxidation catalyzed by Pd-MnO₂ was investigated (Fig. S4†). The HMF conversion and FDCA yield increased linearly with catalyst dosage (20–100 mg). This result can be attributed to an increase in the number and availability of catalytically active sites. Fig. S4(b)† shows the conversion of HMF and yield of FDCA as a function of HMF dosage. When the HMF amount increased from 60 mg to 80 mg, HMF conversion and FDCA yield maintained the maximum values of 100% and 88.1%, respectively. By further increasing HMF loading, to 140 mg, the conversion of HMF declined to 78% and the yield of FDCA dropped to 56.4%.

To elucidate the role of gaseous oxygen in the reaction, we conducted the oxidation of HMF in an Ar atmosphere. The conversion of HMF reached ~10% at 2 h and was unable to proceed afterwards. The reaction rate for HMF oxidation in Ar was determined as 5.7 mol $\text{mol}_{\text{Pd}}^{-1}$, which is ten times lower than that under an O_2 atmosphere (50.8 mol mol $_{Pd}^{-1}$). Such a large difference suggests that gaseous oxygen participated in the oxidation of HMF. To further verify this, we investigated the effect of O₂ pressure on conversion of HMF. If the gaseous oxygen acted as the main oxygen source for the product, a positive relationship between HMF conversion and O₂ pressure should be observed. Indeed, HMF conversion rose from 62.3% to 100% when increasing the O₂ pressure from 0.1 MPa to 1.0 MPa, as shown in Fig. S5.[†] The influence of O₂ pressure became weak when the pressure was above 1.0 MPa, since the O_2 supply was in large excess.

Kinetic fitting of the reaction profiles (Fig. 4(a and b)) was carried out to estimate the reaction pathway and determine the rate-limiting step. The fitting details are provided in the ESI.[†] Table S3[†] gives the estimated rate constants for Pd-MnO₂ and PdNP/MnO₂ and the kinetic model reveals that the rate constants for oxidation of HMF to HMFCA (k_1) and DFF (k_2) are relatively small. Considering that k_2 is higher than k_1 , the catalytic oxidation of HMF to FDCA proceeded preferentially through the pathway as HMF \rightarrow DFF \rightarrow FFCA \rightarrow FDCA, in

Catalyst	HMF/Pd (mole ratio)	O ₂ pressure (MPa)	Conversion of HMF (%)	Yield of FDCA (%)	FDCA productivity (mmol $h^{-1} g_{Pd}^{-1}$)
Pd-MnO ₂	48.74	0.1	100	88.1	100.91 (this work)
PdNP/MnO ₂	28.63	0.1	100	67.8	45.57 (this work)
MnO_2	_	0.1	42.9	30.1	_ `
Commercial Pd/C	0.13	0.1	100	76.6	22.98 (this test)
0.81Pd@PECN	100	0.1	98.4	65.9	27.87^{a} (ref. 67)
4Ru/MnO ₂	33.6	2.4	100	99.1	32.92^{b} (ref. 34)
$2.5 Pd/\gamma$ -Fe ₂ O ₃	10	0.1	92.1	83.0	27.67 ^c (ref. 19)
$1.4 \text{Ru}/\text{Mn}_4\text{Ce}_1\text{O}_Y$	50	1.0	100	84.0	23.09^{d} (ref. 68)

 $\begin{tabular}{ll} \begin{tabular}{ll} Table 1 & Comparison of catalytic performance of Pd-MnO_2, commercial Pd/C and the reported Pd-based catalysts and the reported Pd-based catalysts and the reported Pd-based catalysts are compared are compared are compared are compared and the reported Pd-based catalysts are compared are compared$

Reaction conditions: m(HMF)/m(catalyst) = 0.8, n(HMF): $n(\text{K}_2\text{CO}_3) = 1:4$, water as solvent with an O₂ flow rate of 25 mL min⁻¹, reaction time = 4 h, reaction temperature = 100 °C, 0.1 MPa. ^{*a*} Reaction conditions: HMF = 0.1 mmol, O₂ = 10 mL min⁻¹, K₂CO₃ = 0.4 mmol, water = 2 mL, T = 90 °C, t = 12 h.⁶⁷ ^{*b*} Reaction conditions: HMF = 2 mmol, solvent (H₂O) = 20 mL, t = 10 h, T = 120 °C, P(air) = 2.4 MPa.³⁴ ^{*c*} Reaction conditions: HMF = 0.4 mmol, O₂ balloon, T = 100 °C, t = 12 h.¹⁹ ^{*d*} Reaction conditions: HMF = 2 mmol; solvent (H₂O) = 20 mL; P(air) = 1 MPa, T = 120 °C; t = 18 h.⁶⁸

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which HMF \rightarrow DFF is the rate-limiting step for both catalysts. The rate constants k_1 and k_2 of Pd-MnO₂ are higher than those for PdNP/MnO₂, suggesting higher catalytic activity of Pd-MnO₂. PdNP/MnO₂ has a much higher k_4 value than Pd-MnO₂. This implies that the oxidation of DFF to FFCA for PdNP/MnO₂ was so fast that a tiny amount of DFF was detected in the reaction process. Similar results were obtained by Besson *et al.*⁶⁹

The catalytic stability of atomic and nanosized Pd species supported on α -MnO₂ was tested. The spent catalyst was filtered and washed with deionized water and ethanol and dried at 60 °C overnight, and then used in the repeated test. Pd-MnO₂ catalyst showed no degradation of HMF conversion and FDCA yield after five catalytic cycles (Fig. 4(c)), while nanosized Pd species supported on MnO₂ revealed low catalytic reusability (Fig. 4(d)). TEM characterization of Pd-MnO₂ shows no microstructure changes after five cycles (Fig. S6[†]). The Pd content of used Pd-MnO2 catalyst was determined by ICP-OES and little Pd ($\approx 0.1\%$) had been leached from the catalyst after five runs. The Pd and Mn content in the reactant filtrate were also measured, and the leaching amounts were negligible. The above results suggest that atomic Pd supported on MnO₂ is quite stable in HMF oxidation and could be recycled for five runs without loss of catalytic activity.

3.3. Surface physicochemical analysis

To understand the enhanced catalytic performance of Pd- MnO_2 , we carried out multiple surface chemistry characterizations. XPS was applied to determine the surface elemental composition and valence state of the catalysts. Fig. 5(a) shows the XPS survey scans and peaks corresponding to oxygen,



Fig. 5 (a) XPS survey spectra of Pd-MnO₂, PdNP/MnO₂, and MnO₂; (b) Pd 3d spectra of Pd-MnO₂ and PdNP/MnO₂; (c) O 1s spectra of Pd-MnO₂, PdNP/MnO₂, and MnO₂; (d) O 1s spectra of Pd-MnO₂, PdNP/MnO₂, and MnO₂.

manganese, and palladium are clearly seen in Pd-MnO₂ and PdNP/MnO₂ samples. Fig. 5(b) shows the high-resolution Pd 3d spectra with characteristic Pd $3d_{5/2}$ and $3d_{3/2}$ doublet peaks. The binding energy (BE) of the Pd $3d_{5/2}$ peak position in Pd-MnO₂ is 337.5 eV, which is higher than the BE of Pd²⁺ in bulk PdO (337.2 eV). Such a high positive BE shift has also been observed in the $Pd_x^{2+}Ce_{1-x}O_{2-\delta}$ structure because the ligand environment of Pd²⁺ in the solid solution is different from that in bulk PdO.^{70,71} For the PdNP/MnO₂ sample, the main BE of Pd $3d_{5/2}$ was located at a low value of 336.3 eV, suggesting that the highly dispersed Pd nanoparticles with positive charge resulted from electron transfer from Pd NPs to the MnO₂ surface. Such electron transfer is more pronounced in Pd-MnO₂.

The O 1s spectra were deconvoluted to three peaks corresponding to the lattice O^{2-} (denoted as O_L) at a relatively low binding energy of 529-530 eV, the adsorbed oxygen (denoted as O_{ads}) at 531-532 eV, and the adsorbed water (denoted as $O_{H,O}$) at 532–533 eV (Fig. 5(c)). Considering the fact that oxygen activation is a key step in HMF oxidation, quantification of adsorbed oxygen binding at oxygen vacancies is important in order to understand the catalytic performance.⁷² Therefore, the relative ratio of Oads/(Oads + OL) was used to comprehend the catalytic behavior of all the investigated catalysts towards oxidation reactions. Among them, the Pd-MnO₂ catalyst has a much higher ratio of O_{ads}/(O_{ads} + O_L) (27.1%) than the PdNP/MnO₂ (20.7%) and MnO₂ (13.0%) samples. Fig. 5(d) shows the Mn 3s XPS spectra and the average oxidation state (AOS) of Mn was estimated using the following formula: AOS = 8.956 – 1.126 ΔE_{3s} ,⁷³ where ΔE_{3s} is the binding energy difference between the doublet Mn 3s peaks. The calculated AOS of Pd-MnO₂ is 3.57, which is lower than that of MnO_2 (3.82). This result validates the creation of rich oxygen vacancies upon incorporation of atomic Pd.

H₂-TPR experiments were first performed to investigate the redox properties and metal–support interactions of Pd-MnO₂. In Fig. 6(a), the PdNP/MnO₂ catalyst shows two reduction peaks. One broad peak at 110 °C can be attributed to reduction of the PdO_x species interacting with MnO₂. The second peak at 233 °C is ascribed to the reduction of MnO₂ to MnO. By contrast, only one prominent asymmetric reduction peak is observed for the Pd-MnO₂ catalyst, which can be assigned to the reduction of Pd–O–Mn moieties, followed by reduction of the MnO₂ support. Compared with PdNP/MnO₂, the reduction temperature of oxidized Pd species in Pd-MnO₂ shifts to a higher value (157 °C), owing to the enhanced metal–support interaction.⁷⁴ Meanwhile, the reduction peak of the support shifts to lower temperature, indicative of enhanced reducibility.

O₂-TPD characterization was employed to further investigate the oxygen species and the results are displayed in Fig. 6(b). Generally, the O₂-TPD spectra can be separated into three regions: low temperature (<230 °C), medium temperature (230–470 °C), and high temperature (>470 °C), which correspond to desorption of oxygen species adsorbed on the surface, surface lattice oxygen and bulk lattice oxygen, respectively.⁷⁵



Fig. 6 $H_2\mbox{-}TPR$ (a) and $O_2\mbox{-}TPD$ (b) of $Pd\mbox{-}MnO_2$ and $PdNP\mbox{/}MnO_2$ catalysts.

Compared with PdNP/MnO₂, the Pd-MnO₂ sample released larger amounts of surface-adsorbed oxygen species, as can be seen from the desorption peak at 208 $^{\circ}$ C.

Therefore, combining the XPS results, it is reasonable to deduce that Pd-MnO₂ has larger oxygen vacancies for the adsorption and activation of molecular oxygen. Furthermore, desorption of surface lattice oxygen from the Pd-MnO₂ sample is greater, as seen in the region of medium temperature, indicating the improved mobility of surface lattice oxygen.

In brief, the XPS, H_2 -TPR, and O_2 -TPD results demonstrated that there is a strong metal–support interaction in the Pd-MnO₂ and the presence of atomic Pd activates the lattice oxygen of the support and facilitates the creation of rich oxygen vacancies. These properties are believed to be favorable for HMF oxidation.

3.3. DFT calculation for Pd-species-dependent HMF oxidation

Density functional theory (DFT) calculations were performed to elucidate the origin of the high catalytic activity of Pd-MnO₂. Fig. 7 shows the stable adsorption configurations of the HMF molecule on Pd-MnO₂ and Pd₁₃/MnO₂. It should be noted that the Pd₁₃ cluster supported by MnO₂ was modeled as an approximation for PdNP/MnO2, due to the huge computational demand of simulating PdNP. It can be seen that the distance between the HMF and Pd single atom is 2.05 Å, while the distance between the HMF and Pd_{13} is longer (2.14 Å). This suggests that the Pd single site has stronger binding affinity for HMF, which can be further verified by the calculated adsorption energies. As listed in Table 2, Pd-MnO₂ has a higher adsorption interaction energy of -3.34 eV compared with Pd_{13}/MnO_2 (-2.79 eV). In addition, the C-O bond in HMF is stretched from 1.23 Å to 1.27 Å, indicative of activation of the HMF molecule after adsorption onto Pd-MnO₂. The elec-



Fig. 7 Geometric structures of HMF adsorbed onto the activated Pd site supported on the α -MnO₂ (110) surface. (a) Free HMF in vacuum. (b) HMF adsorbed on Pd-MnO₂. (c) HMF adsorbed on Pd₁₃/MnO₂.

Table 2 Adsorption energy (E_{ads}) of HMF on the Pd-MnO₂ (110) and Pd₁₃/MnO₂ (110) surfaces, E_{vacu} , bond lengths of Pd–O in the catalysts and C–O in the HMF, charge distribution changes of Pd and adsorbed HMF molecule. A negative value means losing the electrons and *vice versa*

	$Pd-MnO_2$ (110)	Pd_{13}/MnO_2 (110)
$E_{ads}(eV)$	-3.34	-2.79
$E_{\rm vacu}(eV)$	-0.21	1.78
Pd–O (Å)	2.05	2.14
C–O (Å)	1.27	1.26
Pd charge (e)	-1.63	-0.14
HMF charge (e)	-0.29	-0.08

tronic properties of the catalyst were also investigated. The charge density distribution plot (Fig. S7†) reveals electron transfer from atomic Pd to the support. Based on the Bader charge analysis (Table 2), the Pd single atom (1.63e) lost more electrons than Pd_{13} (0.14e), which is consistent with the XPS result. In consequence, HMF received more electrons from Pd-MnO₂ (0.29e) than from Pd_{13}/MnO_2 (0.08e), respectively. The pronounced electron exchange in Pd-MnO₂ verifies the ease of activation of the HMF molecule.

On the other hand, the promoted HMF oxidation is involved the activation of molecular oxygen dissolved in aqueous solution. It has been shown that the reducible MnO_2 can effectively adsorb and dissociate O_2 ,⁵⁷ since the oxygen vacancies can reduce the band gap and increase the Femi levels of MnO_2 and elongate the O–O band of the adsorbed O_2 .^{57,76–79} We preferentially explored the formation energies of the oxygen vacancy (E_{vacu}) when single Pd or Pd₁₃ were loaded on MnO_2 . Pd-MnO₂ exhibits a notably lower oxygen vacancy formation energy (-0.21 eV) compared with Pd₁₃/MnO₂ (1.78 eV), which indicates that the formation of oxygen vacancies is more favorable in the presence of atomic Pd. This theoretical result agrees well with the increased oxygen vacancy concentration in Pd-MnO₂ as detected by XPS and O₂-TPD results.

The characterization and theoretical results suggest that the atomic dispersion of Pd not only increases the atomic efficiency, but also maximizes the metal-support interactions

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and effectively tunes the electronic properties of the Pd atoms, thereby enhancing their binding affinity to the HMF molecules. Additionally, the presence of substitutional Pd atoms in the MnO₂ promotes formation of rich oxygen vacancies and increases the mobility of surface lattice oxygen, which facilitates oxygen adsorption, dissociation and replenishment. Considering the interface between Pd and MnO2 as active sites, the turnover frequency (TOF_{interface}) value of the FDCA produced can be calculated according to the length of the perimeter of the Pd-MnO2 by assuming a half sphere of Pd species (for calculation details see ESI[†]).^{80,81} The TOF_{interface} of the Pd-MnO₂ catalyst was found to be 0.042 s⁻¹, which is two times higher than that of its nanoparticle counterpart (0.019 s^{-1}) (Table S3[†]). Therefore, we believe the synergy between Pd single atoms and their surrounding sites is the origin of the high catalytic performance of Pd-MnO₂.

4. Conclusions

In summary, we report an atomic Pd catalyst supported on MnO₂ that can actively, selectively, and stably catalyze the oxidation of HMF to FDCA in aqueous media at ambient pressure. The incorporation of atomic Pd into MnO2 created maximized interfacial sites and induced favorable electronic metal-support interactions for activating HMF. On the other hand, Pd doping into the MnO2 framework generated rich oxygen vacancies, which can effectively activate molecular oxygen. Synergistic interactions between atomic Pd and the surrounding sites of the MnO₂ support effectively promote HMF oxidation. We found that Pd-MnO₂ showed higher activity in the production of FDCA (100.91 mmol $h^{-1} g_{Pd}^{-1}$) than its Pd nanoparticle counterpart (45.57 mmol h^{-1} g_{Pd}^{-1}) and state-of-the-art Pd-based catalysts. The activity of Pd-MnO2 remained unchanged after five catalytic runs. Both the experimental and theoretical results suggested synergy between Pd single atoms and their surrounding sites. Our findings provide a new route to rational design of HMF oxidation catalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Z. Jiang acknowledges financial support from the Joint Fund U1732267. X. Li thanks the fund from the Youth Innovation Promotion Association, CAS. X. Liao gratefully acknowledges support from the Open Research Subject of Key Laboratory (Research Base) of Automotive Engineering (No. szjj2017-075), the Food and Biology Technology (No. szjj2017-109, and financial support from the National Natural Science Foundation of China (No. 21706216) and the Young Scholar Project in Xihua University. EXAFS studies were carried out at the BL14W1 beamline in the Shanghai Synchrotron Radiation Facility, 61

Shanghai Institute of Applied Physics, China (2017-SSRF-PT-00257, 16ssrf00787).

References

- 1 Z. H. Zhang and K. J. Deng, ACS Catal., 2015, 5, 6529.
- 2 P. P. Zhao, Y. Y. Zhang, Y. Wang, H. Y. Cui, F. Song, X. Y. Sun and L. P. Zhang, *Green Chem.*, 2018, **20**, 1551.
- 3 G. D. Yadav and R. V. Sharma, *Appl. Catal.*, *B*, 2014, 147, 293.
- 4 Y. B. Wang, K. Yu, D. Lei, W. Si, Y. J. Feng, L. L. Lou and S. X. Liu, *ACS Sustainable Chem. Eng.*, 2016, 4, 752.
- 5 S. Xu, P. Zhou, Z. Zhang, C. Yang, B. Zhang, K. Deng,
 S. Bottle and H. Zhu, *J. Am. Chem. Soc.*, 2017, 139, 14775.
- 6 Z. L. Yuan, B. Liu, P. Zhou, Z. Zhang and Q. Chi, *Catal. Sci. Technol.*, 2018, **8**, 4430.
- 7 Z. H. Zhang and G. W. Huber, *Chem. Soc. Rev.*, 2018, 47, 1351.
- 8 L. Jiang, P. Zhou, C. J. Liao, Z. Zhang and S. Jin, *ChemSusChem*, 2018, **11**, 959.
- 9 Z. H. Li, K. M. Su, J. Ren, D. J. Yang, B. W. Cheng, C. K. Kim and X. D. Yao, *Green Chem.*, 2018, 20, 863.
- 10 D. H. Nam, B. J. Taitt and K. S. Choi, ACS Catal., 2018, 8, 1197.
- 11 N. Mei, B. Liu, J. D. Zheng, K. L. Lv, D. G. Tang and Z. H. Zhang, *Catal. Sci. Technol.*, 2015, 5, 3194.
- 12 C. M. Zhou, W. P. Deng, X. Y. Wan, Q. H. Zhang, Y. H. Yang and Y. Wang, *ChemCatChem*, 2015, 7, 2853.
- 13 D. Lei, K. Yu, M. R. Li, Y. L. Wang, Q. Wang, T. Liu, P. K. Liu, L. L. Lou, G. C. Wang and S. X. Liu, ACS Catal., 2017, 7, 421.
- 14 S. Siankevich, G. Savoglidis, Z. F. Fei, G. Laurenczy, D. T. L. Alexander, N. Yan and P. J. Dyson, *J. Catal.*, 2014, 315, 67.
- 15 X. W. Han, L. Geng, Y. Guo, R. Jia, X. H. Liu, Y. G. Zhang and Y. Q. Wang, *Green Chem.*, 2016, **18**, 1597.
- 16 X. W. Han, C. Q. Li, Y. Guo, X. H. Liu, Y. G. Zhang and Y. Q. Wang, *Appl. Catal.*, A, 2016, 526, 1.
- 17 H. A. Rass, N. Essayem and M. Besson, *Green Chem.*, 2013, 15, 2240.
- 18 B. Liu, Y. S. Ren and Z. H. Zhang, *Green Chem.*, 2015, 17, 1610.
- 19 Z. H. Zhang, J. D. Zhen, B. Liu, K. L. Lv and K. J. Deng, *Green Chem.*, 2015, 17, 1308.
- 20 B. Zou, X. S. Chen, J. J. Xia and C. S. Zhou, J. Chem., 2018, 268, 743.
- 21 Z. Z. Miao, Y. B. Zhang, X. Q. Pan, T. X. Wu, B. Zhang, J. W. Li, T. Yi, Z. D. Zhang and X. G. Yang, *Catal. Sci. Technol.*, 2015, 5, 1314.
- 22 T. Q. Gao, T. Y. Gao, W. H. Fang and Q. E. Cao, *Mol. Catal.*, 2017, **436**, 171.
- 23 Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen and A. Riisager, *ChemSusChem*, 2019, 2, 672.

- 24 N. K. Gupta, S. Nishimura, A. Takagaki and K. Ebitani, *Green Chem.*, 2011, **13**, 824.
- 25 S. G. Wang, Z. H. Zhang, B. Liu and J. L. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 5820.
- 26 J. H. Xie, J. F. Nie and H. C. Liu, *Chin. J. Catal.*, 2014, 35, 937.
- 27 J. Artz and R. Palkovits, ChemSusChem, 2015, 8, 3832.
- 28 K. Ghosh, R. A. Molla, M. A. Iqubal, S. S. Islam and S. M. Islam, *Appl. Catal.*, *A*, 2016, **520**, 44.
- 29 H. Choudhary and K. Ebitani, *Chem. Lett.*, 2016, 45, 613.
- 30 Z. Y. Gui, W. R. Cao, S. Saravanamurugan, A. Riisager, L. F. Chen and Z. W. Qi, *ChemCatChem*, 2016, 8, 3636.
- 31 Z. Gao, R. F. Xie, G. L. Fan, L. Yang and F. Li, *ACS Sustainable Chem. Eng.*, 2017, 5, 852.
- 32 Q. Wang, W. Hou, S. Li, J. Y. Xie, J. Li, Y. Zhou and J. Wang, *Green Chem.*, 2017, **19**, 3820.
- 33 Y. S. Ren, Z. L. Yuan, K. L. Lv, J. Sun, Z. H. Zhang and Q. Chi, *Green Chem.*, 2018, 20, 4946.
- 34 D. K. Mishra, H. J. Lee, J. Kim, H. S. Lee, J. K. Cho, Y. W. Suh, Y. Yi and Y. J. Kim, *Green Chem.*, 2017, 19, 1619.
- 35 H. Yan, C. L. Su, J. He and W. Chen, *J. Mater. Chem. A*, 2018, **6**, 8793.
- 36 H. Yan, H. Cheng, H. Yi, Y. Lin, T. Yao, C. L. Wang, J. J. Li, S. Q. Wei and J. L. Lu, *J. Am. Chem. Soc.*, 2015, 137, 1048.
- 37 S. Yang, J. Kim, Y. J. Tak, A. Soon and H. Lee, *Angew. Chem., Int. Ed.*, 2016, 55, 2058.
- 38 G. Spezzati, Y. Q. Su, J. P. Hofmann, A. D. Benavidez, A. T. DeLaRiva, J. McCabe, A. K. Datye and E. J. M. Hensen, ACS Catal., 2017, 7, 6887.
- 39 P. X. Liu, Y. Zhao, R. X. Qin, S. G. Mo, G. X. Chen, L. Gu, D. M. Chevrier, P. Zhang, Q. Guo, D. D. Zang, B. H. Wu, G. Fu and N. F. Zheng, *Science*, 2016, 352, 797.
- 40 P. X. Liu, Y. Zhao, R. X. Qin, L. Gu, P. Zhang, G. Fu and N. F. Zheng, *Sci. Bull.*, 2018, 63, 675.
- 41 W. K. Xiang, Y. H. Zhao, Z. Jiang, X. P. Li, H. Zhang, Y. Sun, Z. J. Ning, F. P. Du, P. Gao, J. Qian, K. Kato, M. Yamauchi and Y. H. Sun, *J. Mater. Chem. A*, 2018, **6**, 23366.
- 42 Y. Guo, S. Mei, K. Yuan, D. J. Wang, H. C. Liu, C. H. Yan and Y. W. Zhang, *ACS Catal.*, 2018, **8**, 6203.
- 43 B. T. Qiao, A. Q. Wang, X. F. Yang, L. F. Allard, Z. Jiang, Y. T. Cui, J. Y. Liu, J. Li and T. Zhang, *Nat. Chem.*, 2011, 3, 634.
- 44 J. Lin, A. Q. Wang, B. T. Qiao, X. Y. Liu, X. F. Yang, X. D. Wang, J. X. Liang, J. X. Li, J. Y. Liu and T. Zhang, *J. Am. Chem. Soc.*, 2013, 135, 15314.
- 45 H. Miura, K. Endo, R. Ogawa and T. Shishido, *ACS Catal.*, 2017, 7, 1543.
- 46 J. P. Wang, G. K. Han, L. G. Wang, L. Du, G. Y. Chen, Y. Z. Gao, Y. L. Ma, C. Y. Du, X. Q. Cheng, P. J. Zuo and G. P. Yin, *Small*, 2018, 14, 1704282.
- 47 S. Yang, Y. J. Tak, J. Kim, A. Soon and H. Lee, *ACS Catal.*, 2017, 7, 1301.
- 48 X. G. Li, W. T. Bi, L. Zhang, S. Tao, W. S. Chu, Q. Zhang, Y. Luo, C. Z. Wu and Y. Xie, *Adv. Mater.*, 2016, 28, 2427.

- 49 J. C. Liu, Y. G. Wang, J. Li and J. Am, Chem. Soc., 2017, 139, 6190.
- 50 Y. Tang, Y. G. Wang and J. Li, *J. Phys. Chem. C*, 2017, **121**, 11281.
- 51 N. K. Gamboa-Rosales, J. L. Ayastuy, Z. Boukha, N. Bion,
 D. Duprez, J. A. Perez-Omil, E. del Rio and
 M. A. Gutierrez-Ortiz, *Appl. Catal.*, *B*, 2015, 168, 87.
- 52 C. Lin, Y. H. Zhao, H. J. Zhang, S. H. Xie, Y. F. Li, X. P. Li, Z. Jiang and Z. P. Liu, *Chem. Sci.*, 2018, 9, 6803.
- 53 X. W. Han, C. Q. Li, X. H. Liu, Q. N. Xia and Y. Q. Wang, *Green Chem.*, 2017, **19**, 996.
- 54 E. Hayashi, T. Komanoya, K. Kamata and M. Hara, *ChemSusChem*, 2017, **10**, 654.
- 55 A. B. Gawade, A. V. Nakhate and G. D. Yadav, *Catal. Today*, 2018, **309**, 119.
- 56 M. Ventura, F. Nocito, E. de Giglio, S. Cometa, A. Altomare and A. Dibenedetto, *Green Chem.*, 2018, 20, 3921.
- 57 K. Yu, Y. Q. Liu, D. Lei, Y. Z. Jiang, Y. B. Wang, Y. J. Feng, L. L. Lou, S. X. Liu and W. Z. Zhou, *Catal. Sci. Technol.*, 2018, 8, 2299.
- 58 E. Hayashi, Y. Yamaguchi, K. Kamata, N. Tsunoda, Y. Kumagai, F. Oba and M. Hara, J. Am. Chem. Soc., 2019, 141, 890.
- 59 H. S. Yu, X. J. Wei, J. Li, S. Q. Gu, S. Zhang, L. H. Wang, J. Y. Ma, L. N. Li, Q. Gao, R. Si, F. F. Sun, Y. Wang, F. Song, H. J. Xu, X. H. Yu, Y. Zou, J. Q. Wang, Z. Jiang and Y. Y. Huang, *Nucl. Sci. Tech.*, 2015, **26**, 050102.
- 60 H. S. Wei, X. Y. Liu, A. Q. Wang, L. L. Zhang, B. T. Qiao, X. F. Yang, Y. Q. Huang, S. Miao, J. Y. Liu and T. Zhang, *Nat. Commun.*, 2014, 5, 5634.
- 61 A. Bruix, Y. Lykhach, I. Matolinova, A. Neitzel, T. Skala, N. Tsud, M. Vorokhta, V. Stetsovych, K. Sevcikova, J. Myslivecek, R. Fiala, M. Vaclavu, K. C. Prince, S. Bruyere, V. Potin, F. Illas, V. Matolin, J. Libuda and K. M. Neyman, *Angew. Chem., Int. Ed.*, 2014, 53, 10525.
- 62 Y. Q. Su, J. X. Liu, I. A. W. Filot, L. Zhang and E. J. M. Hensen, ACS Catal., 2018, 8, 655.
- 63 Y. H. Peng, Z. G. Geng, S. T. Zhao, L. B. Wang, H. L. Li, X. Wang, X. S. Zheng, J. F. Zhu, Z. Y. Li, R. Si and J. Zeng, *Nano Lett.*, 2018, **18**, 3785.
- 64 H. B. Zhang, G. G. Liu, L. Shi and J. H. Ye, Adv. Energy Mater., 2018, 8, 1701343.
- 65 A. Bruix, K. M. Neyman and F. Illas, J. Phys. Chem. C, 2010, 114, 14202.
- 66 J. X. Liang, Q. Yu, X. F. Yang, T. Zhang and J. Li, *Nano Res.*, 2018, **11**, 1599.
- 67 B. T. Li, Z. Z. He, M. Wang and X. J. Wang, Int. J. Hydrogen Energy, 2017, 42, 5261.
- 68 T. Y. Gao, J. Chen, W. H. Fang, Q. E. Cao, W. P. Su and F. Dumeignil, *J. Catal.*, 2018, **368**, 5.
- 69 H. A. Rass, N. Essayem and M. Besson, *ChemSusChem*, 2015, 8, 1206.
- 70 E. M. Slavinskaya, R. V. Gulyaev, A. V. Zadesenets, O. A. Stonkus, V. I. Zaikovskii, Y. V. Shubin, S. V. Korenev and A. I. Boronin, *Appl. Catal.*, *B*, 2015, **166**, 91.

- 71 R. V. Gulyaev, A. I. Stadnichenko, E. M. Slavinskaya,
 A. S. Ivanova, S. V. Koscheev and A. I. Boronin, *Appl. Catal.*,
 A, 2012, 439, 41.
- 72 D. Jampaiah, V. K. Velisoju, P. Venkataswamy, V. E. Coyle, A. Nafady, B. M. Reddy and S. K. Bhargava, ACS Appl. Mater. Interfaces, 2017, 9, 32652.
- 73 V. P. Santos, O. S. G. P. Soares, J. J. W. Bakker, M. F. R. Pereira, J. J. M. Orfao, J. Gascon, F. Kapteijn and J. L. Figueiredo, *J. Catal.*, 2012, 293, 165.
- 74 H. G. Peng, C. Rao, N. Zhang, X. Wang, W. M. Liu, W. T. Mao, L. Han, P. F. Zhang and S. Dai, *Angew. Chem.*, *Int. Ed.*, 2018, 57, 8953.
- 75 S. P. Rong, P. Y. Zhang, F. Liu and Y. J. Yang, *ACS Catal.*, 2018, **8**, 3435.

- 76 K. Yu, D. Lei, Y. J. Feng, H. C. Yu, Y. Chang, Y. B. Wang, Y. Q. Liu, G. C. Wang, L. L. Lou, S. X. Liu and W. Z. Zhou, *J. Catal.*, 2018, **365**, 292.
- 77 M. F. Camellone and S. Fabris, J. Am. Chem. Soc., 2009, 131, 10473.
- 78 H. T. Chen, J. Phys. Chem. C, 2012, 116, 6239.
- 79 D. X. Yan, J. Y. Xin, Q. Zhao, K. Gao, X. M. Lu, G. Y. Wang and S. J. Zhang, *Catal. Sci. Technol.*, 2018, 8, 164.
- 80 P. Y. Xin, J. Li, Y. Xiong, X. Wu, J. C. Dong, W. X. Chen, Y. Wang, L. Gu, J. Luo, H. P. Rong, C. Chen, Q. Peng, D. S. Wang and Y. D. Li, *Angew. Chem., Int. Ed.*, 2018, 57, 4642.
- 81 Y. Chen, J. Lin, L. Li, B. T. Qjao, J. Y. Liu, Y. Su and X. D. Wang, ACS Catal., 2018, 8, 859.