

Catalysis

Defective Tungsten Oxide Hydrate Nanosheets for Boosting Aerobic Coupling of Amines: Synergistic Catalysis by Oxygen Vacancies and Brønsted Acid Sites

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Adsorption and activation of molecules on a surface holds the key to heterogeneous catalysis toward aerobic oxidative reactions. To achieve high catalytic activities, a catalyst surface should be rationally tailored to interact with both organic substrates and oxygen molecules. Here, a facile bottom-up approach to defective tungsten oxide hydrate (WO_3 : H_2O) nanosheets that contain both surface defects and lattice water is reported. The defective WO_3 · H_2O nanosheets exhibit excellent catalytic activity for aerobic coupling of amines to imines. The investigation indicates that the oxygen vacancies derived from surface defects supply coordinatively unsaturated sites to adsorb and activate oxygen molecules, producing superoxide radicals. More importantly, the Brønsted acid sites from lattice water can contribute to enhancing the adsorption and activation of alkaline amine molecules. The synergistic effect of oxygen vacancies and Brønsted acid sites eventually boosts the catalytic activity, which achieves a kinetic rate constant of 0.455 h^{-1} and a turnover frequency of 0.85 h^{-1} at 2 h, with the activation energy reduced to \approx 35 kJ mol⁻¹. This work provides a different angle for metal oxide catalyst design by maneuvering subtle structural features, and highlights the importance of synergistic effects to heterogeneous catalysts.

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1. Introduction

Heterogeneous catalysis plays an important role in organic synthesis, as it can offer the relative ease of catalyst separation from product stream for continuous chemical processes, as well as more tolerance of extreme operating conditions than homogeneous analogues.^[1–13] Aerobic oxidative reactions are a large group of organic reactions with the addition of oxygen to (and/or the removal of hydrogen from) functional groups using molecular oxygen, which may further trigger coupling of organic molecules.^[1–7] The catalysts for this class of reactions generally contain noble metals such as Pd,^[1–3] Pt,^[4] and Au,^[5,6] whose low abundance and high cost would hinder large-scale applications. For this reason, non-noble-metal oxides have received much attention toward heterogeneous catalysis owing to their natural abundance and



promising prospect.^[8–10] To achieve highly efficient oxidative reactions, tremendous efforts have been made for the activation of O₂ molecules—a vital step in the reactions.^[11–13] The activation of O₂ molecules on a metal oxide surface relies on the creation of coordinatively unsaturated (CUS) sites, which can be accomplished through defect engineering.^[14–16] Most recently, we have demonstrated that the chemisorption of O₂ molecules at the oxygen vacancies enables the transfer of photoexcited electrons to O₂ molecules, producing superoxide radicals in a photocatalytic system.^[11]

Nevertheless, not only oxygen species but also organic molecules should be adsorbed from solvent onto solid surface in such a reaction system. Thus, the adsorption and activation of organic molecules should also be elementary steps in an aerobic oxidative reaction, which can impact on the overall catalytic performance, but have not received sufficient attention. As a heterogeneous reaction takes place at the catalyst surface, material chemists typically maneuver the adsorption of organic molecules by modifying the surface conditions of catalysts.^[17-20] From the viewpoint of electronic or steric effects, this surface modification can be generally performed by integrating the catalysts with additional inorganic materials or organic ligands. Despite the great progress, it would be fundamentally important to explore if the concepts of traditional organic chemistry can be borrowed to maneuver the adsorption of organic molecules on heterogeneous catalysts. For instance, acid/base catalysts have been widely used to tune the interactions between reaction molecules and catalysts in homogeneous organic synthesis, which can be extended to heterogeneous catalysis particularly with solid acid-catalysts. The solid acid-catalysts (e.g., zeolites, metal oxides, and heteropolyacids), which provide surface Lewis and Brønsted acid sites for adsorption and catalysis, can efficiently facilitate various reactions including aromatization,

isomerization, esterification, reforming, and cracking.^[21–23] Thus, creating acid sites on solid surface should be another promising strategy for enhancing molecular adsorption in heterogeneous catalysis.

Herein, we report a facile bottomup approach to defective tungsten oxide hydrate (WO₃·H₂O) nanosheets. Our finestructure characterizations show that the defective WO3·H2O nanosheets contain surface oxygen vacancies and Brønsted acid sites, derived from the surface defects and lattice water, respectively. The defective WO₃·H₂O nanosheets can serve as an excellent catalyst for the thermal-based aerobic couplings for amines to imines. The amines are considered as Lewis bases due to the electron pairs in p-orbitals of N atoms. As such, the adsorption of amine molecules on a catalyst surface is greatly enhanced by the lattice water that serves as the Brønsted acid sites through hydrogen bonds. Meanwhile, oxygen molecules are activated to superoxide radicals at the CUS sites of oxygen vacancies, triggering the oxidation of the adsorbed amine molecules. The locations of lattice water and oxygen vacancies, which serve as the sites for the adsorption of amine molecules and the activation of oxygen molecules, respectively, are neighbored to enable a synergistic effect. As a result, the synergistic effect—a powerful approach to catalysis which acts on two reaction substrates simultaneously to allow efficient reactions^[24–27]—is well achieved by oxygen vacancies and Brønsted acid sites in defective WO₃·H₂O nanosheets. This synergistic catalysis induces significant enhancement on catalytic performance for the aerobic couplings of amines to corresponding imine with a reduced apparent activation energy, as compared with other tungsten oxide (WO₃) and WO₃·H₂O counterparts.

2. Results and Discussion

2.1. Material Characterization

The defective WO₃·H₂O (namely, WOH-D) nanosheets are synthesized by a previous protocol with slight modification using glucose as a reductant.^[11] The reduction by glucose can remove some lattice oxygen atoms to create the defects of oxygen vacancies. The methods for synthesis and characterization are described in detail in the Experimental Section and Supporting Information. X-ray diffraction (XRD, Figure S1, Supporting Information) reveals the phase of product as orthorhombic WO₃·H₂O (JCPDS No. 43-0679). As indicated by scanning and transmission electron microscopy (SEM and TEM, **Figure 1**a,b), the WOH-D nanosheets have uniform morphology with the average edge length of 145.3 \pm 10.8 nm and thickness of 15.1 \pm 1.8 nm (Figure S2, Supporting Information). The lattice structure is further examined



Figure 1. Electron microscopy characterizations of defective $WO_3 \cdot H_2O$ (WOH-D) nanosheets: a) SEM, b) TEM, and c,d) HRTEM images.





Figure 2. Characterizations for oxygen vacancies and lattice water. a) Room-temperature ESR spectra of WOH-D and nondefective $WO_3 \cdot H_2O$ (WOH-ND) nanosheets. The same molar number of the samples was used to normalize the ESR spectra. b) High-resolution W 4f XPS spectra of WOH-D and WOH-ND nanosheets. c) High-resolution O 1s XPS spectra of WOH-D and defective WO_3 (WO_3 -D) nanosheets. d) Solid-state MAS ¹H-NMR spectra of WOH-D and WO₃-D nanosheets.

by high-resolution TEM (HRTEM, Figure 1c). The lattice fringes with spacing of 2.5 and 2.6 Å can be assigned to the (002) and (200) planes of WO₃·H₂O, respectively. Meanwhile, the HRTEM image of a cross section (Figure 1d) shows the (020) lattice spacing of 5.3 Å, suggesting that the flat surfaces of nanosheets are (010) planes.

To identify the defects in nanosheets, room-temperature electron spin resonance (ESR) spectroscopy and X-ray photoelectron spectroscopy (XPS) are both used to characterize the sample, referenced against nondefective WO₃·H₂O (namely, WOH-ND) nanosheets (characterizations are shown in Figures S3-S5, Supporting Information). The WOH-ND nanosheets are prepared through a similar protocol except the absence of reductant glucose. As compared with WOH-ND nanosheets, WOH-D nanosheets exhibit a significant ESR signal at g = 2.002 (shown in Figure 2a) that can be attributed to the electron trapping at oxygen vacancies.^[28] In addition, two characteristic peaks at the binding energies of 35.8 and 38.0 eV can be well assigned to the $4f_{7/2}$ and $4f_{5/2}$ for W⁶⁺, respectively, in the high-resolution W 4f XPS spectra of WOH-ND nanosheets (Figure 2b).^[29] In comparison, the peaks of W $4f_{7/2}$ and $4f_{5/2}$ for WOH-D nanosheets are obviously shifted to 35.4 and 37.6 eV, respectively. The lower binding energies indicate the increase of electron density in W atoms, which further verifies the existence of oxygen vacancies.^[30] According to the peak fitting (Figure 2b), no peaks for lower valence W (W5+ and/or W4+) can be distinguished from the spectra, indicating that the existence of oxygen vacancies insufficiently generates lower-valence

W atoms.^[29,30] Despite their difference in oxygen vacancies, the WOH-D and WOH-ND samples show the same phase and comparable morphology (Figures S3–S5, Supporting Information), indicating that the existence of defects does not cause significant changes in long-distance order. Another evidence for the presence of defects is the change in color and light absorption. As depicted in Figure S6 (Supporting Information), the defects in WOH-D nanosheets enable remarkable near-infrared light harvesting, which is ascribed to the upshifting of valence band maximum (VBM) and the emergence of defect states below the conduction band minimum (CBM).^[11] As a result, the color of WOH nanosheets is altered from bright yellow to deep green by the presence of oxygen vacancies.

Upon identifying the existence of oxygen vacancies, we further employ high-resolution O 1s XPS and solid-state magic-angle-spinning (MAS) ¹H nuclear magnetic resonance (¹H-NMR) spectroscopy to analyze the lattice water in samples. To make reliable assignments on spectroscopic information, we remove the lattice water from WO₃·H₂O samples (i.e., WOH-D and WOH-ND) through calcination at 673 K in Ar atmosphere, which produces two WO₃ samples as references—defective WO₃ (WO₃-D) and nondefective WO₃ (WO₃-ND) nanosheets. The details for the calcination method and the related sample characterizations are shown in the Experimental Section (Supporting Information) and Figures S7–S13 (Supporting Information), respectively. The O 1s XPS spectra of WOH-D nanosheets (Figure 2c) display two peaks at about 530.0 and 532.5 eV, which can be assigned

to the lattice oxygen atoms (Peak A) in metal oxides and the oxygen atoms (Peak B) in lattice water and/or adsorbed oxygen species, respectively.^[31] In comparison, the intensity of Peak B has been substantially reduced for the WO₃-D nanosheets that possess no lattice water but can adsorb oxygen species at surface defects (see the quantitative analysis of O 1s peaks in Table S1, Supporting Information). As a matter of fact, the Peak B almost disappears for the WO₃-ND nanosheets without surface defects (Figure S14, Supporting Information), indicating that the weak Peak B for WO₃-D is mainly attributed to the adsorbed oxygen species at surface defects.^[28,32] The assignment of lattice water in XPS is further confirmed by the comparison between WO₃-ND and WOH-ND (Figure S14, Supporting Information); the addition of lattice water significantly promotes the Peak B.

Another evidence for lattice water is provided by solidstate MAS ¹H-NMR spectroscopy. As displayed in Figure 2d, the ¹H-NMR spectrum of WOH-D exhibits a strong signal at 6.08 ppm of chemical shift, corresponding to the W–OH bonds for lattice water, which can generally serve as a Brønsted acid.^[33] In sharp contrast, the peak at 6.08 ppm almost disappears for WO₃-D. Similarly, the 6.08 ppm signal has been observed for WOH-ND rather than WO₃-ND nanosheets (Figure S15, Supporting Information), confirming that the



chemical shift of 6.08 ppm originates from lattice water. The shoulder peak at 4.69 ppm of chemical shift is attributed to the water molecules^[34] (Figure S16, Supporting Information) mainly adsorbed at defect sites, so this peak is almost unrecognizable for the WOH-ND and WO₃-ND samples without surface defects (Figure S16, Supporting Information).

2.2. Catalytic Performance

The information gleaned above demonstrates that WOH-D nanosheets contain both defect-rich surface and lattice water. We are now in a position to investigate their synergistic effect on catalytic performance. Here, we take aerobic couplings of amines as a model reaction to reflect the functions of synergistic sites on the interactions with O_2 and organic substrate molecules. The adsorption and activation of O_2 molecules can be enhanced at oxygen vacancy sites,^[11,15] while the amine molecules are the Lewis bases that well interact with Brønsted acid sites—lattice water. The design is anticipated to enable a synergistic catalysis in aerobic couplings of amines.

The initial catalytic assessments are performed at 353 K using oxygen molecules as an oxidant. As a model substrate (illustrated in **Figure 3**a), 4-methyl-benzylamine (1A)



Figure 3. Catalytic performance in aerobic coupling of 4-methyl-benzylamine. a) Schematic illustration for the aerobic coupling. b) Time-dependent catalytic conversion. c) The kinetic rate plots and calculated kinetic rate constants (*k*). d) The calculated turnover frequencies (TOFs) based on the data at 2 h. e) The Arrhenius plots and calculated apparent activation energies (E_a). Reaction conditions: catalyst (0.4 mmol), 4-methyl-benzylamine (1 mmol), solvent (CH₃CN, 5 mL), O₂ (0.2 MPa), temperature (353 K). The conversion is determined by GC-MS using benzotrifluoride as an internal standard. The kinetic rate constants (*k*) are calculated through first-order reaction equation. The apparent activation energies (E_a) are obtained by Arrhenius equation at various temperatures (313, 323, 333, and 353 K).

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is first oxidized to 4-methyl-benzaldehyde (2A) and eventually coupled into the corresponding imine (2B) as a final product.^[13,35] We perform the catalytic performance evaluation using various catalysts, while no products are detected in the absence of catalysts (Table S2, Supporting Information, Entry 1). Figure 3b shows the time-dependent catalytic conversion over WOH-D and WO₃-D nanosheets. Apparently WOH-D nanosheets can offer higher catalytic activity in the total conversion of 1A to 2B, and the conversion can be completed within 8 h. WOH-D nanosheets convert 1A up to 69% at 2 h and 92% at 6 h, whereas only 24% and 46% conversion is achieved by WO₃-D nanosheets, respectively (shown in Table S2, Supporting Information, Entry 2-5). As both WOH-D and WO₃-D nanosheets possess surface oxygen vacancies, the lattice water in WOH-D nanosheets turns out to be the key to boosting the catalytic activity. The catalytic activities of both WOH-D and WO₃-D are strongly dependent on reaction temperatures (Table S2, Supporting Information, Entry 6–11). Notably, the reaction can be well triggered by our WOH-D nanosheets with a 43% conversion at 6 h as the temperature is reduced as low as 313 K (Table S2, Supporting Information, Entry 6), demonstrating the excellent catalytic activity. Moreover, nondefective samples (i.e., WOH-ND and WO₃-ND nanosheets) are also employed to assess the activity for catalyzing aerobic coupling of 1A. However, both can hardly trigger the reaction, and only trace amounts of **2B** are detected (Table S2, Supporting Information, Entry 12 and 13). which indicates the necessity of surface oxygen vacancies.

Regarded as a pseudo-first-order reaction.^[35] the aerobic coupling of amines is quantified with the kinetic rate plots as illustrated in Figure 3c. The calculated kinetic rate constant (k)for WOH-D nanosheets reaches 0.455 ± 0.032 h⁻¹, six times higher than that of WO₃-D nanosheets $(0.072 \pm 0.004 \text{ h}^{-1})$. Moreover, the turnover frequencies (TOFs) of the catalysts are calculated at the reaction time of 2 h, as demonstrated in Figure 3d. The TOF of WOH-D nanosheets reach 0.85 h⁻¹, substantially higher than that of WO₃-D nanosheets (0.30 h^{-1}) . Table S3 (Supporting Information) compares the TOF of our WOH-D nanosheets with the recently reported data for heterogeneous catalysts in the aerobic couplings of amines to imines by both thermal-based and light-driven catalysis. The TOF by our WOH-D catalyst is comparable to those of most efficient catalysts that can achieve similar selectivity. To further understand the reaction process, apparent activation energies (E_a) are calculated using the Arrhenius equation based on the kinetic rate constants at various temperatures (Equation (1)):

$$\ln k = \ln A - \frac{E_{\rm a}}{RT} \tag{1}$$

where E_a is apparent activation energy, k is kinetic rate constant, T is absolute temperature, A is pre-exponential factor, and R is molar gas constant. As shown in Figure 3e, the E_a for WOH-D nanosheets is dramatically lower (35.01 ± 4.67 kJ mol⁻¹ vs 52.21 ± 4.82 kJ mol⁻¹ for WO₃-D nanosheets), indicating that less energy is required to surmount the energy barrier.

The synergistic catalysis by Brønsted acid and oxygen vacancy sites can provide a generic approach to the aerobic couplings of various benzylamine derivatives with high

conversion and selectivity. To demonstrate the niche of our WOH-D nanosheets, we have examined the aerobic couplings of various amines under the optimized conditions (Table 1). Both electronic effect (Table 1, Entry 1–5) and steric effect (Table 1, Entry 3, 6 and 7) induced by the substituents can be well tolerated. Meanwhile, our WOH-D catalyst also exhibits excellent conversion and selectivity for heterocyclic amines to imines (Table 1, Entry 8 and 9). Remarkably, the WOH-D nanosheets can catalyze the aerobic couplings of aliphatic amines with high conversion and selectivity (see Table 1, Entry 10 and 11) in addition to aromatic amines, which is generally considered more challenging due to the inactive α -H of aliphatic amine.^[13] Another important parameter for catalyst is durability. Our durability tests (Figures S17-S20, Supporting Information) show that the catalytic performance decreases in catalytic cycles due to the consumption of surface defects, while the lattice water can be well maintained. Nevertheless, the consumed surface defects can be readily recovered to boost the catalytic performance back up through a simple reduction process.^[36]

2.3. Mechanism Investigation

The catalytic results above indicate that the samples containing surface defects can efficiently tune on the reactions, while the nondefective samples cannot (Table S2, Supporting Information, Entry 3, 5, 12, and 13). In literature, the activation of O_2 molecules is generally considered as a key step to limit the catalytic performance of aerobic oxidative reactions.^[11-13] Previous studies have revealed that the O2 molecules can be chemisorbed and activated at the CUS sites created by oxygen vacancies.^[15] To correlate O₂ activation with oxygen vacancies, we employ ESR to resolve the activated oxygen species—superoxide radicals (O2^{•-}) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent.^[37] As illustrated in Figure 4a,b, when WOH-D or WO₃-D nanosheets are used as catalysts (blue lines), the ESR signals show a nearly 1:1:1:1 quartet patterns-the characteristic fingerprints of spin adducts derived from DMPO-O2 •-, demonstrating the generation of O2 . In comparison, both WOH-ND and WO3-ND nanosheets are incapable of generating O2 •-, as no signals are detected in ESR spectra (green lines). As such, the activation of O_2 molecules into $O_2^{\bullet-}$ species should rely on the surface oxygen vacancies in our case.

To confirm the formation of $O_2^{\bullet-}$ species, superoxide dismutase (SOD) is used as a scavenger to quench $O_2^{\bullet-}$ during the ESR detection.^[37] As shown in Figure S21 (Supporting Information), the intensity of ESR signals dramatically decreases for both WOH-D and WO₃-D nanosheets after adding SOD, suggesting that $O_2^{\bullet-}$ is the activated oxygen species formed in our system. Furthermore, as the spin adduct of DMPO- $O_2^{\bullet-}$ has a relatively short lifetime, we employ a more stable spin trapping agent 5-(diethylphosphono)-5-methyl-1-pyrroline N-oxide (DEPMPO) to examine the formation of $O_2^{\bullet-}$.^[38] As depicted in Figure S22 (Supporting Information), the ESR spectra for both WOH-D and WO₃-D nanosheets show the characteristic pattern for DEPMPO- $O_2^{\bullet-}$ with similar intensities, further proving their comparable ability



Entry ^{a)}	Substrate	Product	Conv. [%]	Select. ^{b)} [%]
1	NH ₂		93	98
2	NH ₂		99	97
3	NH ₂		99	98
4	F NH2	F N C F	98	99
5	CI-NH2		88	98
6	NH ₂		99	93
7	NH ₂		99	96
8	NH ₂	OT N TO	94	99
9	NH ₂	S N S	76	99
10	NH ₂		77	90
11	NH ₂		89	81

Table 1. Catalytic performance in the aerobic coupling of various amines to imines using WOH-D nanosheets as a catalyst.

^{a)}Reaction conditions: WOH-D nanosheets (0.4 mmol), substrate (1 mmol), solvent (CH₃CN, 5 ml), O₂ (0.2 MPa), temperature (353 K), reaction time (8 h). The conversion (Conv.) and selectivity (Select.) are determined by GC-MS using benzotrifluoride as an internal standard; ^{b)}Main by-products: corresponding aldehyde, nitrile, and oxime.

for O₂ activation. In addition, we also verify the key role of O₂^{•-} species in the aerobic coupling of amines by employing p-benzoquinone (p-BQ) and 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy (TEMPOL) as scavengers.^[39,40] As shown in Figure S23 (Supporting Information), the catalytic activity in the aerobic coupling of 4-methyl-benzylamine is significantly suppressed by quenching O₂^{•-} with p-BQ or TEMPOL, indicating that the O₂^{•-} species indeed participates in the aerobic coupling of amines.

To further look into the role of surface oxygen vacancies in O₂ activation, we examine the adsorption configurations of O₂ molecule on the surface of perfect and defective WO₃·H₂O (see the surface structural models in Figure S24, Supporting Information) by first-principles simulations. As illustrated in Figure S25a (Supporting Information), O₂ molecule cannot be chemisorbed on the perfect surface due to the lack of adsorption sites. In sharp contrast, the surface oxygen vacancies can perfectly serve as the chemisorption sites for O₂ molecule through an end-on chemisorption configuration, and the surface H atoms can hardly alter the O₂ adsorption (Figure S25b, Supporting Information). The high simulated adsorption energy (E_{ad}) of -0.82 eV (vs -0.01 eV for perfect surface) suggests the substantially enhanced chemisorption

of O_2 on defective surface, which would induce efficient O_2 activation during the reaction process.

The results mentioned above clearly demonstrate the role of oxygen vacancies in the catalytic reactions. Nevertheless, it still remains elusive why WOH-D nanosheets can offer the significantly enhanced catalytic activity as compared with WO₃-D. Although WOH-D nanosheets possess an inferior ability for O₂ adsorption than WO₃-D nanosheets as indicated by adsorption isotherms (Figure S26, Supporting Information), the two catalysts have a comparable capability of activating O2 molecules into O2 - species based on the intensity of ESR signals (Figure 4a,b, blue lines). The amount of generated $O_2^{\bullet-}$ is the key parameter to catalytic performance associated with O2 molecules.[11-13] In addition, we have excluded the possible influence of surface areas and crystal phases on catalytic performance: 1) the WOH-D and WO3-D nanosheets possess comparable surface areas, as shown in Figure S27 (Supporting Information); 2) although the WOH-D and WO₃-D possess different crystal phases due to the loss of lattice water, both (010) surfaces consist of distorted WO₆ octahedrons by sharing corners with analogous atomic arrangements (Figure S7, Supporting Information).^[41] For this reason, we then examine the other reaction SCIENCE NEWS www.advancedsciencenews.com



Figure 4. ESR detection of superoxide radicals using a DMPO spin-trapping agent with a) $WO_3 \cdot H_2O$ samples and b) WO_3 samples. The * labels a nearly 1:1:1:1 quartet pattern corresponding to the characteristic fingerprints for the spin adducts derived from DMPO- $O_2^{\bullet-}$. DRIFTS spectra for the chemisorption of c) pyridine and d) benzylamine molecules on WOH-D and WO_3 -D nanosheets. The background spectra have been subtracted from the DRIFTS spectra of the adsorbed molecules. The adsorption configurations of benzylamine molecule on the surface of e) defective $WO_3 \cdot H_2O$ (i.e., WOH-D) and f) defective WO_3 (i.e., WO_3 -D) with the computed adsorption energy.

component—the adsorption of amine molecules at the catalyst surface.

The interaction between substrate molecules and catalyst surface generally plays a vital role in tuning catalytic performance.^[18–20] As mentioned above, the lattice water in $WO_3 H_2O$ supplies W–OH bonds, whose H atoms at surface can serve as a typical Brønsted acid.^[33] The ¹H-NMR signal at the chemical shift of 6.08 ppm by WOH-D nanosheets (Figure 2d) indicates that the catalyst surface possesses strong Brønsted acidity.^[42] To further verify the acidity, we employ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) to examine the catalyst using pyridine as a probe molecule. As shown in Figure 4c, the peaks at 1455, 1575, and 1608 cm⁻¹ are ascribed to the chemisorption of pyridine at surface Lewis acid sites, while the peak at 1538 and

1637 cm⁻¹ can be attributed to Brønsted acid sites. Meanwhile, the 1496 cm⁻¹ signal is induced by both Lewis acid and Brønsted acid sites.^[43,44] The Lewis acid sites originate from the unsaturated tungsten atoms created by defect engineering.^[45,46] Notably, WOH-D nanosheets exhibit distinct Brønsted acid sites as compared with WO₃-D nanosheets. Given WOH-D and WO₃-D nanosheets possess comparable morphologies and defect concentrations, the Brønsted acid sites on WOH-D nanosheets should be designated by the W–OH bonds associated with lattice water. As a further evidence, the Brønsted acid sites have also been well identified for WOH-ND nanosheets (Figure S28, Supporting Information).

The Brønsted acidity of WO₃·H₂O would enable better adsorption of Lewis-base amines through hydrogen bonds.

Figure S29 (Supporting Information) depicts the adsorption isotherms of benzylamine on catalysts. The fitting results based on the Langmuir equation (Table S4, Supporting Information) demonstrate that WOH-ND nanosheets can adsorb substantially more benzylamine molecules than WO₃-D under the catalytic condition. Furthermore, DRIFTS spectra (Figure 4d) clearly reveal the chemisorption of benzylamine on the surface of WOH-D and WO₃-D catalyst. After adsorbing benzylamine molecules, WOH-D nanosheets exhibit recognizable peaks at 1454, 1495, 1590, and 1603 cm⁻¹, which are assigned to the adsorbed benzylamine. Specifically, the peaks at 1454 and 1603 cm⁻¹ are indexed to the bending vibrations of C-H and N-H bonds, respectively,^[47,48] while the bands at 1495 and 1590 cm⁻¹ are associated with the stretching vibrations of benzene ring.^[49] In comparison with WOH-D, the corresponding peaks are much weaker for WO₃-D nanosheets. This indicates that the interaction between benzylamine and WOH-D nanosheets is substantially stronger than WO₃-D nanosheets. Moreover, as compared with free benzylamine molecules (1606 cm^{-1} in Figure S30, Supporting Information), the bending vibration of N-H bonds is slightly red-shifted, which suggests that the formation of hydrogen bonds can alter the strength of N-H bonds and facilitate their activation. Our control experiments (Figure S31, Supporting Information) reveal that WOH-ND nanosheets can also well adsorb benzylamine molecules whereas WO₂-ND hardly works. This further confirms that lattice water instead of surface defects is responsible for the enhanced adsorption of benzylamine on catalyst surface.

To further gain insight into the amine-catalyst interaction, we conduct first-principles simulations to examine the adsorption of benzylamine to the surface of defective WO₃·H₂O (i.e., WOH-D, Figure S24b, Supporting Information) and defective WO₃ (i.e., WO₃-D, Figure S32, Supporting Information). As shown in Figure 4e, the lattice water of WOH-D supplies Brønsted acid sites so that benzylamine molecules can be efficiently adsorbed via the hydrogen bonds between the Brønsted acid sites and N atoms of benzylamine. In contrast, the adsorption of benzylamine to WO₃-D surface can only take place through the bonding of H atoms (benzylamine) to surface O atoms (WO₃-D) (Figure 4f), more weakly than that of Brønsted acid sites. As a result, the E_{ad} of benzylamine on the surface of WOH-D and WO₃-D are -1.27 and -1.13 eV, respectively. This suggests the stronger interaction of benzylamine with WOH-D surface, which would facilitate the activation of substrate molecules for enhanced catalytic efficiency. To further correlate catalytic performance with the adsorption and activation of substrate molecules, we take benzyl alcohol as the substrate to carry out oxidative reactions under the same condition. As hydroxyl group (-OH) is not as a strong Lewis base as amino group (-NH₂), the Brønsted acid sites on WOH-D nanosheets cannot efficiently facilitate the adsorption and activation of benzyl alcohol. As a result, the addition of lattice water can hardly alter the catalytic activity (see Figure S33, Supporting Information). This control experiment further unravels the role of Brønsted acid sites in boosting catalytic performance.

Taken together, the experimental and theoretical results above clearly depict the synergistic catalysis by oxygen





Scheme 1. Schematic illustrating the synergistic catalysis for aerobic couplings of amines to imines by oxygen vacancies and Brønsted acid sites on the surface of defective $WO_3 \cdot H_2O$ nanosheets.

vacancies and Brønsted acid sites in defective WO_3 ·H₂O nanosheets. As illustrated in **Scheme 1**, the lattice water provides Brønsted acid sites for efficiently adsorbing amine molecules via strong hydrogen bonds. The enhanced adsorption can facilitate the oxidation of amine molecules by the superoxide species whose generation relies on the CUS sites created by oxygen vacancies. This synergistic effect eventually boosts the catalytic activity of WOH-D nanosheets for the aerobic coupling of amines. The aerobic coupling reactions undergo the pathway below (Equations (2)–(5)):^[13,35]

$$O_2 \xrightarrow{e^-} O_2^{\bullet-}$$
(2)

$$Ph \xrightarrow{\quad \text{``}} Ph \xrightarrow{\quad \text{+'}} Ph \xrightarrow{\quad \text{+'}} NH_2$$
(3)

$$Ph \xrightarrow{\bullet} H_2 \xrightarrow{\bullet} Ph \xrightarrow{\bullet} H_2 \xrightarrow{\bullet} Ph \xrightarrow{\bullet} H_3 \xrightarrow{\bullet} Ph \xrightarrow{\bullet} O \xrightarrow{$$

$$Ph$$
 NH_2 + Ph O H_2 Ph N Ph (5)

In this process, the activated O_2 molecules oxidize amine molecules (chemisorbed at the neighbored lattice water) and combine H atoms to generate H_2O_2 as an intermediate product. This process does not involve the dissociation of O–O bonds. The H_2O_2 molecules can spontaneously decompose to H_2O and O_2 . To verify this process, we employ a well-established *N*,*N*-diethyl-*p*-phenylenediamine (DPD)/ horseradish peroxidase (POD) method to detect the produced H_2O_2 .^[50] As shown in Figure S34 (Supporting Information), the formation of H_2O_2 intermediate has indeed been observed.

3. Conclusion

In summary, we have developed a facile bottom-up approach to the defective WO_3 ·H₂O nanosheets that contain surface oxygen vacancies and Brønsted acid sites. The oxygen vacancies can provide coordinatively unsaturated sites for activating oxygen molecules into superoxide radicals-a key component for triggering reactions. More importantly, the existence of Brønsted acid sites induces significant changes in catalytic performance. The strong interaction between Lewis-base amine molecules and Brønsted-acid catalyst surface facilitates the adsorption and oxidation of amine molecules. As a proof of concept, the synergistic effect of oxygen vacancies and Brønsted acid sites at the surface of WOH-D nanosheets enables sixfold enhancement on aerobic couplings of amines against the catalysts in the absence of lattice water, in terms of kinetic rate constants. The WOH-D catalyst achieves a calculated TOF of 0.85 h^{-1} at 2 h and a reduced activation energy down to ≈ 35 kJ mol⁻¹. This strategy can work for not only aromatic amines but also aliphatic amines with inactive α -H. The work reported here calls for future efforts on catalyst design at molecular level, and demonstrates the necessity of looking into subtle surface features of catalytic materials.

4. Experimental Section

Materials: Sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$, 99.5%), citric acid (CA, 99.5%), SOD, p-BQ (97%), TEMPOL (98%), DPD (98%), and POD were purchased from Aladdin. DMPO (98%) was purchased from Adamas-beta. DEPMPO (98%) was obtained from TCI. D(+)-glucose (AR), hydrochloric acid (HCl, 36–38%), sodium borohydride (NaBH₄, AR), acetonitrile (CH₃CN, AR), and anhydrous ethanol (EtOH, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. All amines and benzyl alcohol for catalytic experiments were obtained from Energy Chemical. The water used in all experiments was deionized (DI). All of the chemical reagents were used as received without further purification.

Synthesis of $WO_3 \cdot H_2O$ Nanosheets: The defective $WO_3 \cdot H_2O$ nanosheets were synthesized through a facile hydrothermal method. Briefly, 1.0 mmol of Na2WO4·2H2O and 1.5 mmol of CA were added into 30 mL of H₂O to produce a transparent solution. Then 10 mmol of glucose was added into the solution as a reductant. After vigorous stirring for 10 min, 3 mL of HCl (6 M) was added into the mixed solution, followed by another 30 min stirring. The mixture was transferred into a 50 mL Teflon-lined autoclave, sealed, and heated at 393 K for 24 h. After the autoclave had cooled down to room temperature, the product was separated by centrifugation, washed with H₂O and EtOH for several times until the organics were completely removed, and then dried at 333 K in a vacuum oven for 24 h for further use and characterization. The defects in the samples can be tailored by changing the amount of glucose, and nondefective $WO_3 \cdot H_2O$ nanosheets were synthesized using the same method except the absence of glucose.

Catalytic Measurements for Aerobic Couplings of Amines: The catalytic reactions were carried out in CH_3CN solution in O_2 atmosphere at various temperatures. Typically, 1 mmol of amine and 0.4 mmol of catalyst were dispersed in 5 mL of CH_3CN in a pressure bottle, which was then filled with 0.2 MPa of O_2 and sealed. The reaction was performed in an oil bath for different time at desired temperature with magnetic stirring. After the completion of reaction, the catalyst was removed by filtration. 0.5 mL of the resultant solution was taken and diluted to 5 mL by CH_3CN . The final solution was analyzed by gas chromatography-mass spectrometry

(GC-MS, 7890A and 5975C, Agilent) using benzotrifluoride as an internal standard. The TOF was calculated using Equation (6):

$$TOF = \frac{n_0 \times C \times S}{n_{cat} \times t}$$
(6)

where n_0 is the initial molar number of substrate, *C* and *S* are the conversion and selectivity at the reaction of *t*, n_{cat} is the molar number of catalyst, and *t* is the reaction time.

DRIFTS Spectroscopy Characterizations: The DRIFTS measurements for pyridine and benzylamine chemisorption were performed using a Bruker IFS 66v Fourier transformation spectrometer with a Harrick diffuse reflectance accessory at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) in National Synchrotron Radiation Laboratory (NSRL), Hefei. The catalyst samples were first pretreated at 353 K for 2 h under vacuum, and a background spectrum was obtained from 1700 to 1400 cm⁻¹ before adsorbing the pyridine or benzylamine molecules. Then 10 µL of pyridine or benzylamine was injected into the samples. After reaching the adsorption equilibrium, the samples were retreated at 353 K for 4 h under vacuum to completely remove the physically adsorbed molecules. Finally, the DRIFTS spectra for pyridine or benzylamine chemisorption were collected. The background spectra were subtracted from the DRIFTS spectra of adsorbed species.

First-Principles Simulations: The simulations were performed based on spin-polarized density functional theory (DFT) using the VASP package.^[51,52] Perdew–Burke–Ernzerhof (PBE) exchangecorrelation functional within a generalized gradient approximation (GGA) and the projector augmented-wave (PAW) potential were employed.^[53] The Brillouin zone was sampled with Monkhorst-Pack generated sets of k-points, $10 \times 5 \times 10$ k-point mesh was chosen for bulk computations, and $5 \times 5 \times 1$ k-point mesh for surface computation. All geometric structures were fully relaxed until energy and forces were converged to 10^{-5} eV and 0.02 eV Å⁻¹, respectively. The calculated lattice parameters of the WO₃·H₂O unit cell are a = 5.25 Å, b =10.71 Å, and c = 5.13 Å. A system of 2 × 2 slab consisting of seven layers was employed to model the surface of $WO_3 \cdot H_2O$ (010) with oxygen atom and H₂O terminated, in which three top atom layers are relaxed and four atom layers are fixed to the bulk positions during the geometry optimizing simulations. The periodic boundary condition was set with a 18 Å vacuum region above the plane of $WO_3 \cdot H_2O$ (010). For the WO₃ simulation, the lattice structure was used by a previous model.^[11] The monoclinic structure of WO₃ with 8 W and 24 O atoms in a primary unit cell was built, and the calculated lattice parameters are a = 7.49 Å, b = 7.66 Å, c = 7.84 Å, and $\beta = 90.3^{\circ}$. A system of 2 × 2 slab with four layers was employed to model the WO_3 (010) surface, with oxygen atom terminated. Three top layers were relaxed from the bulk positions during the geometry optimizing. The periodic boundary condition was set with a 18 Å vacuum region above surface. All the atom sites of adsorbates (i.e., benzylamine and O₂ molecules) on $WO_3 \cdot H_2O$ (010) or WO_3 (010) were relaxed to investigate the interaction between adsorbates and $WO_3 \cdot H_2O$ (010) or WO_3 (010).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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