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Recent advances in the strategies of developing water-resistant catalysts for the removal of atmospheric pollutants

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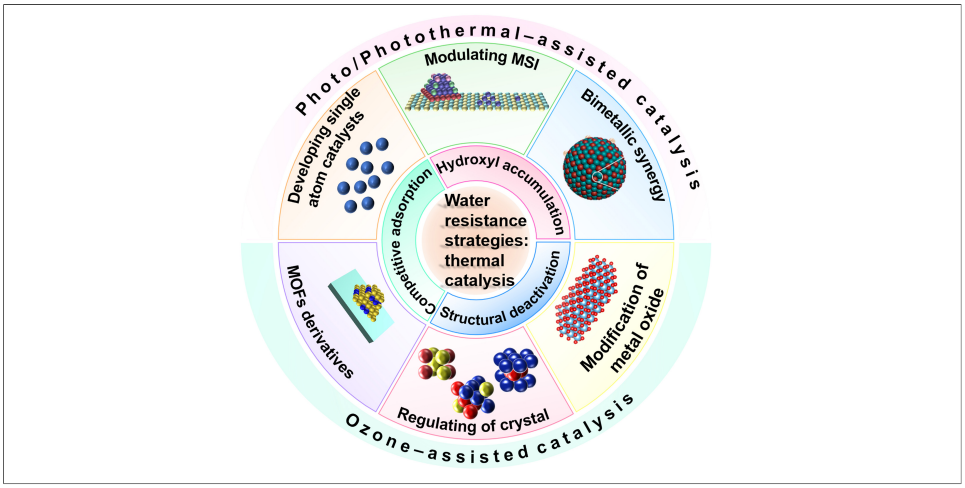

Abstract

In the catalytic oxidation of atmospheric pollutants such as volatile organic compounds (VOCs), catalyst deactivation induced by water under realistic operating conditions has emerged as a critical bottleneck constraining the large-scale application of this technology. This review aims to provide a systematic global perspective for developing highly efficient and water-resistant catalytic materials for the oxidation of atmospheric pollutants. First, the underlying mechanisms of water-induced catalyst deactivation in humid atmospheres are dissected in depth from the perspectives of micro-kinetics and thermodynamics, and critical evolution processes including competitive adsorption initiated by polar water molecules, poisoning by surface persistent hydroxyl groups, blockage of active oxygen recycling, and irreversible hydrothermal reconstruction on the macroscale are systematically delineated. Subsequently, recent frontier materials design strategies to enhance the water resistance of catalysts are reviewed, with emphasis place on elucidating the structure-activity relationships behind the development of single-atom catalysts,

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modulation of metal-support interactions (MSI), exploitation of bimetallic synergy, modification of metal oxides, regulation of crystal structures, and utilization of metal-organic framework (MOF) derivatives, as well as photo/photothermal and ozone-assisted catalysis. Finally, the core challenges associated with the current water-resistant catalytic technologies for their industrialization are summarized, aiming to provide solid theoretical support for rational research.

INTRODUCTION

With the acceleration of global industrialization and urbanization, some activities, such as industrial production, fossil fuel combustion, and vehicular emissions, have released massive quantities of atmospheric pollutants, including nitrogen oxides (NO*x*), volatile organic compounds (VOCs), methane, carbon monoxide, and particulate matter. These pollutants not only trigger severe ecological and environmental problems (e.g., photochemical smog and regional haze), but also pose profound threats to human health, which brings up a critical global challenge requiring urgent environmental remediation[1,2]. Among numerous frontier purification technologies, catalytic oxidation has established its mainstream status in the field of atmospheric pollution control, owing to its core advantages, including mild reaction conditions, high CO_2 selectivity, good purification efficiency, broad applicability, and absence of secondary pollution. Consequently, it has been widely implemented in practical scenarios, such as selective catalytic reduction of NO_x with ammonia (NH_3-SCR), VOC oxidation, and low-temperature CO elimination for the treatment of industrial flue gases[3].

In the practical application of gas-solid heterogeneous catalytic systems, however, the presence of water is the critical bottleneck constraining catalytic efficiency and long-term operation stability[4,5]. Since practical industrial flue gases, combustion exhaust, and ambient air universally contain moisture with a certain concentration (typically in the range of 1-20 vol%), the catalyst surface is inevitably surrounded by humid gas[6]. Under this complex interfacial chemical environment, water molecules not only act as reaction media participating in energy transfer, but also profoundly intervene in the catalytic cycle as highly polar "competitors". In fact, among numerous classic heterogeneous catalytic systems for environmental and energy utilization, water-induced performance degradation has become a ubiquitous challenge in the field[7]. For instance, water molecules occupying acid sites and inducing dealumination of the zeolite framework are the primary cause of catalyst deactivation in the NH_3-SCR reaction[8]. In the automotive three-way catalysis (TWC) and low-temperature CO oxidation, the irreversible accumulation of surface hydroxyl groups blocks the noble metal active centers, thereby significantly elevating the thermodynamic energy barrier for oxygen activation[9]. In energy conversion reactions (e.g., CO_2 hydrogenation and methane reforming), the active phase sintering induced by the hydrothermal environment is the greatest impediment limiting their industrial applications.

Compared to simple small molecules (e.g., CO and NO), catalytic VOC oxidation processes exhibit even more severe and complex sensitivity to moisture[10]. From the perspective of micro-kinetics, highly polar water molecules undergo fierce competitive adsorption with VOCs at active sites and are dissociated on the catalyst surface to form persistent hydroxyl species (-OH*) that are difficult to desorb, consequently blocking the surface active oxygen cycle and interfacial charge transfer process. From the macroscale of materials, long-term exposure of catalysts to hydrothermal environments readily triggers irreversible structural reconstructions [e.g., sintering and agglomeration of active metal particles, collapse of support pore structures, and failure of strong metal-support interactions (SMSI)].

As global standards for atmospheric pollutant emissions become increasingly stringent, effectively overcoming the inhibitory effect of moisture has emerged as an essential path toward the industrial implementation of highly efficient purification technologies[11]. Current frontier research is dedicated to reshaping the surface microenvironment in humid atmospheres via precise regulation of the physicochemical properties of the catalysts (e.g., surface polarity and oxygen vacancy concentration as well as interfacial geometric and electronic struc-

tures), thereby achieving highly efficient removal of atmospheric pollutants under complex operating conditions[12-15].

Based on this background, this review aims to provide a systematic and in-depth global perspective for developing catalytic materials with excellent water resistance for atmospheric pollutant oxidation. Firstly, Section 2 starts from the perspective of micro-kinetics and thermodynamics, profoundly analyzing the underlying mechanisms of water-induced catalyst deactivation. It comprehensively states critical dynamic evolution processes triggered by water molecules, including interfacial competitive adsorption, poisoning by persistent surface hydroxyls, blockage of the active oxygen cycle, and hydrothermal reconstruction under long-term operation conditions. Subsequently, Section 3 presents catalyst design strategies aimed at enhancing the intrinsic water resistance of the catalysts. It focuses on elucidating the structure-activity relationships behind the construction of single-atom and bimetallic sites, support modifications, defect engineering, surface hydrophobic modifications, and porous confinement effects based on metal-organic frameworks (MOFs). Furthermore, Section 4 systematically evaluates external-field-assisted enhancement technologies (such as photocatalysis, photothermocatalysis, and catalytic ozonation), revealing their deep reinforcement mechanisms in overcoming the kinetic energy barriers of water molecule desorption, triggering radical cascades, and completely reconstructing reaction pathways. Finally, Section 5 summarizes the core challenges of current water-resistant catalytic technologies facing their large-scale industrial applications. It provides forward-looking perspectives on multi-pollutant synergistic governance under realistic complex operation conditions, applications of advanced operando dynamic characterization technologies, and establishment of standardized evaluation systems, aiming to provide solid theoretical support for the rational catalyst design and engineering scale-up of next-generation industrial-grade and all-weather water-resistant purification technologies. In this review, we focus specifically on water-induced deactivation as the key bottleneck under realistic humid conditions; highlight the continuous evolution chain from competitive adsorption to hydroxyl accumulation and finally to hydrothermal structural reconstruction; integrate catalyst intrinsic design, interfacial regulation, and external-field enhancement into one unified framework; and place special emphasis on water-resistance strategies with stronger relevance to practical wet industrial conditions.

WATER-INDUCED DEACTIVATION MECHANISMS

The negative impact of water on catalysts does not manifest as a simple linear decline in catalytic activity. Instead, it profoundly reshapes the physicochemical environment of the catalytic interface through multiple pathways, including competitive adsorption, surface hydroxyl formation, blockage of the active oxygen cycle, and active phase reconstructions[16].

Competitive adsorption

In the catalytic oxidation of atmospheric pollutants, VOC molecules typically need to be first adsorbed at active sites of the catalyst, subsequently undergoing the steps of C–H bond activation, oxygen insertion, and deep oxidation of intermediates. In a humid atmosphere, water molecules often prioritize interaction with surface metal sites, acid-base sites, and oxygen vacancies by virtue of their smaller kinetic diameter, extremely rapid diffusion rate, and strong polar characteristics. This severely inhibits the effective adsorption of VOC molecules at physical and weak chemical levels. Furthermore, oxygen vacancies can play multiple roles: (i) facilitating adsorption and activation of O_2 and some pollutant molecules; (ii) influencing water adsorption and dissociation behavior; (iii) accelerating lattice oxygen migration and promote the Mars-van Krevelen (MvK) mechanism; and (iv) either improving catalytic turnover frequencies by enhancing oxygen mobility or becoming the sites for excessive hydroxyl accumulation, depending on their concentration and local environment under humid conditions. Therefore, oxygen vacancies have a dual role, and their beneficial effect depends on balanced defect density, neighboring coordination structure, and hydroxyl removal kinetics.

The advantage of water molecules in adsorption competition is fundamentally determined by the hydrophilicity of the surface microenvironment and the site charge distribution. For example, water molecules very easily occupy oxygen vacancies on the catalyst surface, giving rise to a sharp reduction

in the number of active sites available for activating gaseous oxygen molecules. This, in turn, causes a substantial decrease in the abundance of active oxygen (e.g., O_2^-, O_2^{2-}, O^-, *etc.*) species within the reaction system, ultimately hindering the deep oxidation of organic intermediates to CO_2[17]. Furthermore, different types of active centers exhibit variations in their water adsorption modes. For catalytic systems following the Langmuir-Hinshelwood (L-H) mechanism, where both VOCs and oxygen require pre-adsorption, the aggressive intervention of water will simultaneously block the two critical initial steps of VOC substrate enrichment and oxygen activation[18].

It is noteworthy that the deactivation solely caused by the competitive adsorption of molecular water usually exhibits strong reversibility[19]. Numerous studies have demonstrated that introducing water vapor in the low-temperature range leads to a significant decrease in VOC conversion, but upon cutting off the moisture provision, catalytic activity often rapidly restores to its initial level. At higher temperatures, however, because the desorption thermodynamics of water are more favorable and the relative adsorption strength of target reactants (e.g., oxygen and aromatic hydrocarbons) at the active sites is enhanced, the inhibitory effect of water weakens significantly[20]. This temperature dependence and the activity recovery after cutting off water vapor provision fully demonstrate that the catalyst deactivation at this stage primarily stems from dynamic surface physical occupancy rather than substantial damage to the catalyst structure. Therefore, targeting this type of reversible inhibition, weakening water adsorption by constructing hydrophobic interfaces or regulating surface polarity is an effective strategy[21].

Surface hydroxyl accumulation and blockage of the active oxygen cycle

On numerous oxide supports or metal-oxide interfaces, the interference of water molecules is not limited to instantaneous adsorption in the molecular state. They tend to undergo dissociation at defect sites or metal centers, forming surface -OH* with strong chemical bonding. Compared to molecular water, these hydroxyl species possess extremely high desorption energy barriers and are prone to irreversible accumulation on the catalyst surface, thereby triggering persistent site passivation. This signifies that the deeper hazard of moisture lies in the transformation of water molecules into the chemical "poisons" that are difficult to eliminate [Figure 1][22].

The inhibitory mechanism of the substantial accumulation of surface hydroxyls on the catalytic oxidation of VOCs is primarily manifested in three dimensions: (i) The direct blocking of active sites. Strongly bound hydroxyls can persistently occupy precious metal active centers and oxygen vacancies at the metal-support interface, completely cutting off the contact channels for VOCs and O_2; (ii) The blockage of the active oxygen cycle [failure of the MvK mechanism]. In the classical MvK mechanism, gas-phase oxygen molecules are activated at oxygen vacancies to replenish the consumed lattice oxygen species. Hydroxyl coverage not only significantly raises the activation energy for oxygen molecule adsorption and cleavage but also hinders the generation of highly active oxygen (e.g., superoxide and peroxide) species, causing the entire catalytic cycle to stagnate due to "oxygen deficiencies"; (iii) The reshaping of the local microenvironment and reaction pathways. The substantial accumulation of hydroxyls alters the local electronic structure (e.g., *d*-band center shift), surface acidity or basicity, and even the hydrogen-bonding network of the catalytic interface. This alteration not only increases the desorption difficulty of intermediates but is also highly prone to inducing side reaction pathways, giving rise to the deposition of multi-carbon intermediates (e.g., formates and acetates) on the surface that would increase the risk of coking poisoning[23,24].

Owing to the extreme difficulty of hydroxyl desorption at low temperatures and the slow rates of bulk lattice oxygen migration and surface regeneration, the poisoning effect triggered by hydroxyl accumulation manifests a particularly severe degree under low-temperature and high-humidity operating conditions[25]. Therefore, the activity retention rate of a catalyst under the conditions of low-temperature and high-humidity often reflects its intrinsic resistance to hydration poisoning more accurately.

Hydrothermal reconstruction and structural deactivation

After long-term irreversible damage beyond the reversible or semi-reversible inhibition caused by surface adsorption and hydroxylation, the catalysts undergo profound microstructure evolution in long-

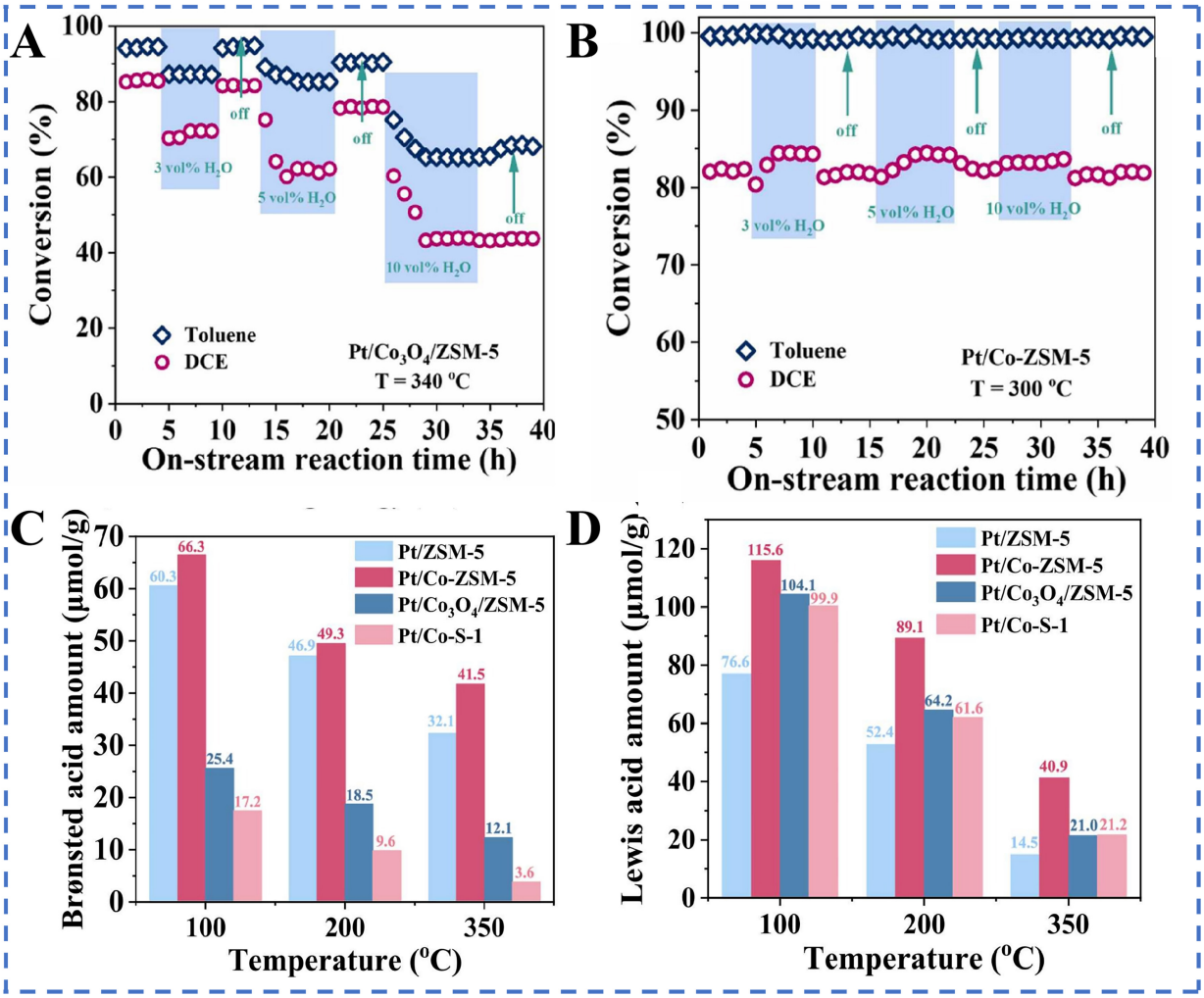

Figure 1. (A and B) Toluene or DCE conversion as a function of on-stream reaction time in the presence or absence of H_2O over (A) Pt/Co_3O_4/ZSM-5 and (B) Pt/Co-ZSM-5 at SV = 40,000 mL/(g·h); (C) Brønsted acid amount and (D) Lewis acid amount of the catalysts as a function of temperature[22]. This figure is quoted with permission[22]. Copyright 2025, Elsevier. DCE: Dichloromethane; SV: space velocity.

term humid and hot service environments, triggering complete irreversible catalyst deactivation. This process is generally referred to as "hydrothermal reconstruction", which involves surface dissolution-redeposition, crystal phase transformation, sintering of the active phases, and disintegration of the metal-support interfaces.

For supported precious metal (e.g., Pt, Pd, or Ru) or transition metal catalysts, high-temperature water vapor can significantly weaken the SMSI. The intervention of water molecules lowers the migration barrier of metal surface atoms, accelerating the Ostwald ripening and particle agglomeration processes. This directly gives rise to a sharp reduction in metal dispersion and the disappearance of low-coordination, high-activity sites, with catalytic intrinsic activity and water resistance subsequently suffering a cliff-like decline[26].

For oxide supports, long-term exposure to moisture not only triggers deep bulk hydroxylation but also permanently passivates intrinsic surface defect sites (e.g., oxygen vacancies), causing them to lose crucial oxygen storage/release and oxygen-exchange capacities. Furthermore, in some porous materials (e.g., zeolites, MOF derivatives, or mesoporous metal oxides) with high surface areas, the hydrothermal stress can cause micropore blockage, pore wall shrinkage, or even overall collapse of the framework architecture, fundamentally cutting off the mass transfer channels[27]. The weakly adsorbed surface hydroxyls are generally more reversible and can be desorbed upon changing atmosphere or tempera-

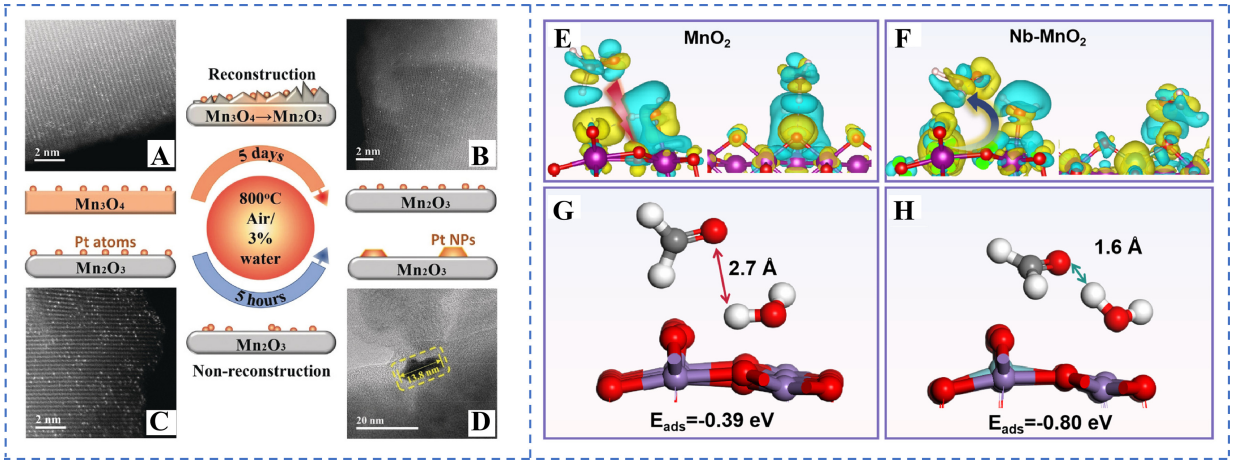

Figure 2. (A) AC-STEM image of Pt_1/Mn_3O_4; (B) AC-STEM image of Pt_1/R-Mn_2O_3-5D obtained via calcining Pt_1/Mn_3O_4 at 800 °C in air with 3 vol% water vapor for 5 days; (C) AC-STEM image of Pt_1/Mn_2O_3; (D) HRTEM image of Pt_{NP}/Mn_2O_3-5H obtained via calcining Pt_1/Mn_2O_3[32]; (A-D) adapted with permission from reference[32]. Copyright 2020, John Wiley and Sons. Charge density difference of HCHO and H_2O on (E) MnO_2 and (F) Nb-MnO_2. Adsorption configurations of HCHO and H_2O on (G) MnO_2 and (H) Nb-MnO_2[33]; (E-H) adapted with permission from reference[33]. Copyright 2026, John Wiley and Sons. AC-STEM: Aberration-corrected scanning transmission electron microscopy; HRTEM: high-resolution transmission electron microscopy.

ture; however, the strongly bound lattice hydroxyls are more persistent and more closely associated with irreversible blockage of oxygen migration and the MvK pathway. Moreover, these methods provide multi-dimensional analytical means for clarifying dynamic behaviors of the catalytic surface active sites: (i) operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to monitor hydroxyl vibration bands and their dynamic evolution; (ii) near-ambient-pressure X-ray photoelectron spectroscopy (XPS) to track chemical-state changes of surface oxygen and hydroxyl species; and (iii) *in situ* Raman and infrared spectroscopy (IR) isotope-labeling experiments to distinguish the adsorbed water-derived species from the lattice-involved hydroxyls.

In summary, water-induced catalyst deactivation is not a single event but a continuous dynamic evolution process "from surface to bulk and from reversible to irreversible": In the initial stage, water molecules lead to rapid depletion of the active sites through competitive adsorption of reactants and water; subsequently, the surface hydroxyls generated by dissociation of water deeply lock oxygen cycles and interfacial charge transfer; and after long-term hydrothermal accumulation, this surface inhibition eventually evolves into fatal structural deactivation, such as particle sintering, support hydroxylation, and framework collapse. Therefore, enhancing the water resistance of catalysts must not rely on the blind optimization of a single parameter, but rather on comprehensive defensive design around the entire chain mechanism of "competitive adsorption-hydroxyl poisoning-structural reconstruction". Based on this, the next section presents the key material design strategies developed in recent years for improving the water resistance of catalytic VOC oxidation.

CATALYST DESIGN STRATEGIES FOR ENHANCING WATER RESISTANCE IN CATALYTIC OXIDATION OF VOCS

Developing single-atom catalysts

Single-atom catalysts (SACs), by virtue of their ultimate atom utilization efficiency, well-defined local coordination environments, and unique electronic structures, exhibit revolutionary potential in the field of water-resistant catalysis[28,29]. Compared to conventional nanoparticle (NP) catalysts, the most prominent water-resistance mechanism of single-atom sites is first manifested in the "spatial isolation" of their geometric structures [Figure 2A-D][30-32].

At the level of electronic structure and local microenvironment, the water-resistance advantage of single atoms further stems from their ability to finely regulate adsorption priority and reaction

pathways. Single atoms are typically highly coordinated to oxides, carbon-based, or zeolite frameworks in the form of M-O, M-N, etc., and this coordination-induced strong charge transfer can significantly reshape the local electronic structure of the metal center. By regulating the electron cloud density of the isolated sites, the strong chemisorption of polar water molecules at such low-coordination sites can be effectively weakened, while retaining the activation ability towards target VOCs and oxygen. More significantly, specific metastable coordination structures can proactively alter the evolution pathway of water from a thermodynamic perspective [Figure 2E-H][33]. For instance, in some meticulously designed metastable single-atom (e.g., Pt_1/TiO_2) systems, the special local structure not only enhances lattice oxygen mobility to safeguard the smooth operation of the MvK mechanism but also transforms the dissociation process of H_2O from an endothermic reaction to an exothermic reaction, thereby facilitating the *in situ* dissociation of water into the highly active -OH*[34].

In long-term service environments with high humidity and high temperatures, catalysts are highly prone to hydrothermally induced active-phase reconstruction and agglomeration or sintering. Numerous studies have indicated that precisely confining precious metal single atoms within lattice defects (e.g., abundant oxygen vacancies) of the support not only forms robust M–O bonding, but this SMSI also kinetically increases the migration energy barrier of metal atoms and effectively weakens the adsorption of H_2O at the metal active sites[35]. Furthermore, encapsulating single atoms within the micropores of zeolites (e.g., silicalite-1 zeolite) with specific topology or constructing core-shell structures with microscopic physical barriers using ultrathin silica shells (e.g., constructing Pt-O-Si active interfaces) can generate a strong synergy with the confinement microenvironment of the support[36,37]. This dual protection mechanism of chemical anchoring and physical confinement induces a favorable redistribution of the interfacial electronic structure, optimizes surface acidity, and promotes gas-phase oxygen activation. Consequently, it achieves exceptional stability and ensures that the active sites are atomically dispersed even under harsh conditions, such as high water vapor concentrations (> 10 vol%) and severe hydrothermal aging[38].

Modulating MSI

Despite the rapid development of SACs in recent years, metal nanoparticles, by virtue of their high-density surface active sites, outstanding substrate activation capabilities, and mature loading processes, remain the most widely applied active phase system in the field of catalytic VOC oxidation at present[39]. Therefore, a primary focus in designing water-resistant nanoparticle systems is identifying the optimal size window that balances substrate activation kinetics with hydrothermal stability[40].

Aside from particle size, MSI is the focal point determining the water-resistant behavior of nanoparticles. The catalytic oxidation of VOCs typically does not occur independently on a pure metal surface but relies heavily upon the synergistic microenvironment at the junction between the metal and the support. Under humid conditions, interfacial charge transfer can significantly change the electron density of the noble metal surface [Figure 3][41]. By precisely regulating the interfacial electronic structure (for instance, constructing MnO_x/Pt heterojunctions[42], selectively loading Ru on the SnO_2/CeO_2 mixed oxide surface[43], or constructing Pt-WO_3 active interfaces), strong electronic coupling interactions can be induced at the interfaces[44]. This reconfiguration of electron arrangements can effectively weaken the stable adsorption of polar water at the active sites while maintaining efficient activation of oxygen and VOC molecules. Furthermore, excellent interfaces often possess powerful oxygen migration and oxygen vacancy regeneration capabilities. When water molecules inevitably occupy part of the interfacial sites, the support, which is rich in oxygen vacancies, can continuously provide lattice oxygen or highly active oxygen species for the reaction via the rapid oxygen migration from the subsurface or interface, thereby effectively compensating for the damaged MvK oxygen cycle path due to the physical blocking by water molecules[45].

Under long-term humid and hot service conditions, SMSI and spatial confinements constitute the final line of defense for nanoparticle systems against "hydrothermal reconstruction and sintering". A high-humidity environment can accelerate the migration of active metals, giving rise to the permanent loss of low-coordination high-activity sites. To overcome this fatal flaw, researchers "anchor" nanoparticles by

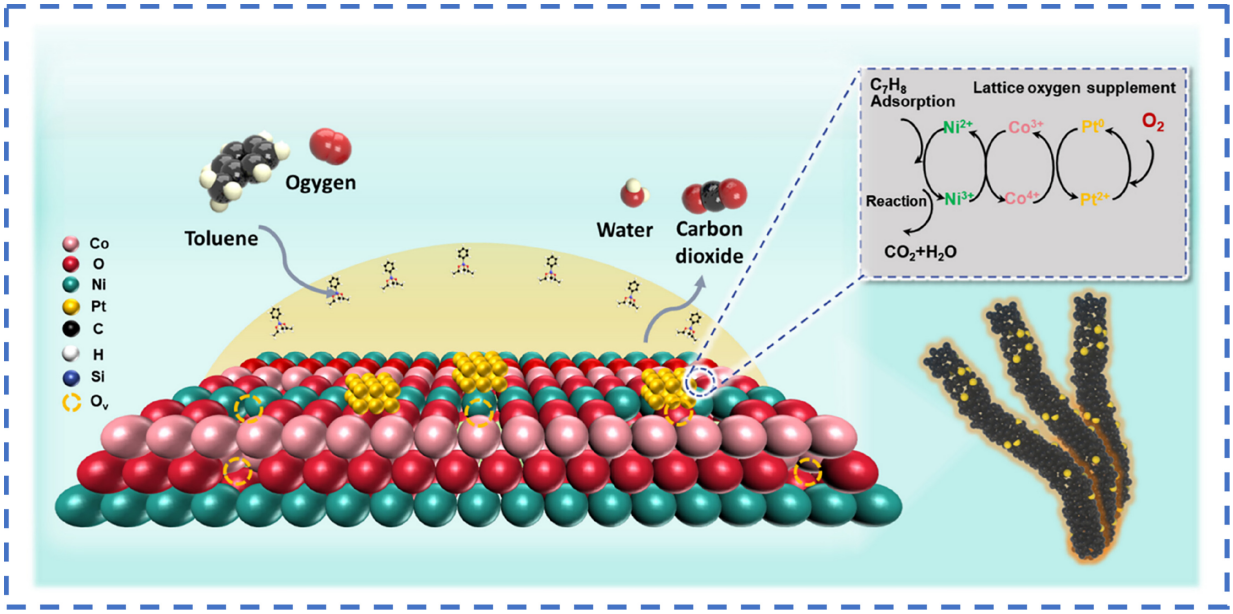

Figure 3. Schematic illustration of the reaction mechanism for the oxidation of VOCs[41]. This figure is reproduced from reference[41] under the Creative Commons CC BY License. VOCs: Volatile organic compounds.

constructing physical confinement structures or strengthening chemical bonding. For example, using mesoporous zeolite shells to physically encapsulate the Pt-CeO_2 active components, this porous network not only plays a role in steric hindrance and hydrophobic buffering for water molecules but also tightly confines them within microscale channels, fundamentally suppressing Pt particle sintering induced by high-temperature water vapor and endowing the material with excellent hydrothermal stability[27,46]. In addition, modifying supports (e.g., Al_2O_3) by introducing heteroatoms like Si can significantly enhance the thermal stability of the carrier and strengthen the interaction between the noble metal and the carrier, effectively maintaining the high dispersion and water resistance of the nanoparticles[47]. However, interfacial regulation similarly needs to follow the classic Sabatier rule. Therefore, seeking a delicate balance between the site exposure rate and the interfacial anchoring strength is key to maximizing the water resistance of the metal nanoparticles.

Metal doping and bimetallic synergy

In single-metal or single-metal oxide systems, because active sites are uniform, catalysts often struggle to simultaneously achieve high intrinsic activity and excellent water-resistant stability under humid working conditions. Competitive adsorption, hydroxyl accumulation, and structural degradation triggered by polar water molecules significantly amplify the intrinsic shortcomings of single-metal catalysts. To this end, introducing heterogeneous doping elements or constructing bi- or multi-metallic synergistic systems has become a key strategy for reshaping the surface reaction ecology at the atomic and molecular scales and enhancing the overall toughness of the catalytic network[48].

First, electronic-structure reconstruction and differential adsorption regulation are the most fundamental microscopic mechanisms of the bimetallic strategy. Due to differences in electronegativity, valence state, and orbital energy levels between heterogeneous metals, strong local charge transfer is inevitably triggered at the interface or within the alloy phase. This redistribution of the local electron cloud can precisely shift the *d*-band center of the active metal, fundamentally changing the affinity of surface sites for different adsorbed species [Figure 4][23]. Under hot and humid working conditions, rational electronic regulation can effectively weaken the coordination bond strength between polar water and the active center, reducing the probability of deep dissociation of water and the formation of continuous hydroxyl networks. For example, by introducing specific heterogeneous metals around the active metal (e.g., constructing multi-element coupling structures)[49,50], it is possible not only to inhibit the

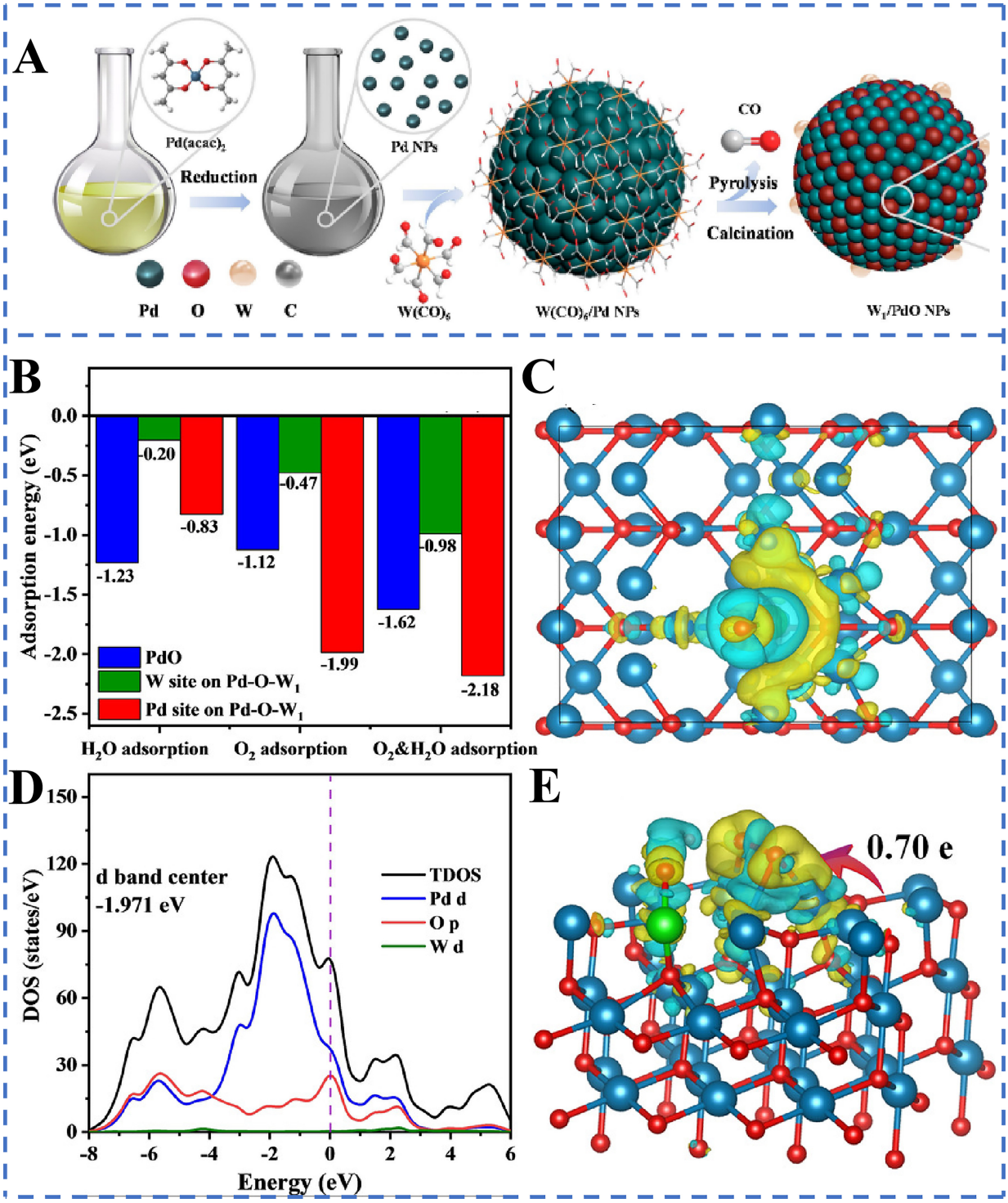

Figure 4. (A) Schematic illustration of the preparation process of PdW_1/Al_2O_3; (B) Adsorption energies of the adsorbates on the surface of PdO and Pd-O-W_1; (C) Charge density difference of the Pd-O-W_1 structure. Yellow and cyan colors represent the accumulation and loss of electron density, respectively; (D) Total density of states for Pd-O-W_1; (E) Charge density difference of the Pd-O-W_1 catalyst under the adsorption of H_2O and O_2[23]. This figure is quoted with permission[23]. Copyright 2022, John Wiley and Sons. DOS: Density of states.

full coverage of active sites by water molecules but also to alter the adsorption configuration of water via directional electron transfer. While ensuring the preferential adsorption of VOCs and oxygen, this imparts an extremely high selective tolerance towards water molecules on the catalyst surface[51].

Second, dynamic defect engineering and oxygen cycle compensation are core to maintaining reaction continuity in the presence of moisture. In the pro-

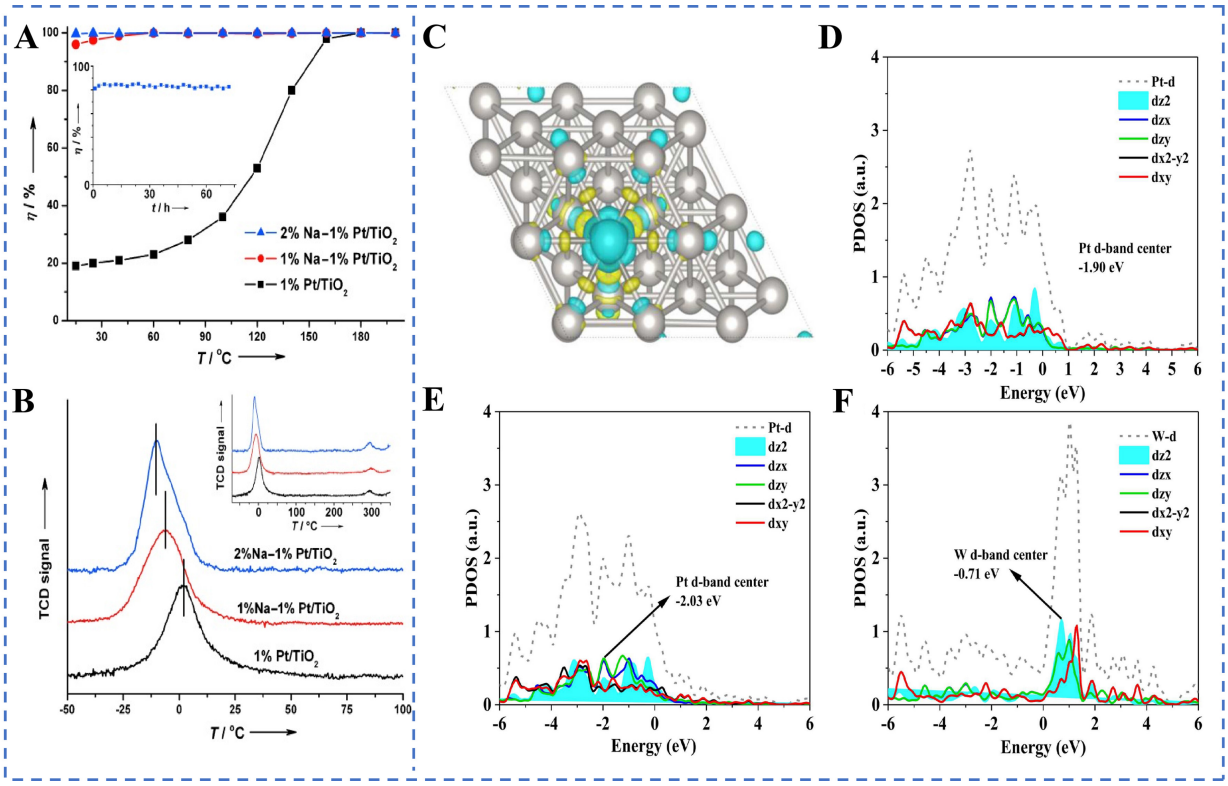

Figure 5. (A) HCHO conversion (η) as a function of temperature (T) over x wt% Na-1 wt% Pt/TiO_2 (x = 0, 1, and 2). Reaction conditions: 600 ppm HCHO, 20 vol% O_2, 50% relative humidity, He (balance), total flow rate = 50 cm^3/min, and SV = 120,000 h^{-1} (inset: stability test over 2 wt% Na-1 wt% Pt/TiO_2 at 25 °C and SV = 300,000 h^{-1} under the same other reaction conditions); (B) H_2-TPR profiles of x wt% Na-1% Pt/TiO_2 (x = 0, 1, and 2)[54]. (A and B) adapted from reference[54]. Copyright 2012, John Wiley and Sons; (C) Electron density difference plots for the Pt-W structure. Blue represents an electron-loss region, and yellow represents an electron-accumulation region. The isosurface level is 0.01 e/Å^3; PDOS plots for the (D) Pt sites in Pt nanoparticles, (E) Pt sites in PtW nanoparticles, and (F) W sites in PtW nanoparticles[62]. C–F adapted from reference[62]. Copyright 2026, Elsevier. PDOS: Projected density of states; H_2-TPR: hydrogen temperature-programmed reduction.

cess of VOC oxidation following the MvK mechanism, water vapor directly cuts off the supply chain of lattice oxygen by strongly occupying the surface oxygen vacancies. Metal doping (such as introducing heterogeneous cations with ionic radii or valence state mismatch into transition metal oxides[22,52], and even alkali metal ions like Na^+[53-57], K^+[58,59], or rare earth ions like Y^+[60], *etc.*) can induce strong microscopic distortion within the lattice, thereby directionally generating defect sites in large quantities [Figure 5A and B][49,54]. These customized defects not only substantially promote oxygen mobility within the lattice but also open up low-barrier activation channels for gaseous oxygen that are independent of water molecules. We emphasize that heavier alkali metals can tune the electronic environment of neighboring noble-metal sites, influence surface basicity and oxygen activation pathways, modify adsorption/desorption behavior of water and aromatic pollutants, in some cases, facilitate deep oxidation of molecules such as toluene under high-humidity conditions when combined with suitable noble-metal/-transition-metal interfaces. At the same time, we note that the beneficial effect depends strongly on loading amount, dispersion, and interfacial structure, and excessive alkali addition may also suppress activity.

Finally, the decoupling of surface reaction paths and functional division effectively breaks through the catalytic limits of single sites. In complex humid systems, if multiple tasks (e.g., adsorbing substrates, dissociating oxygen molecules, and scavenging surface hydroxyls) are highly concentrated at the same active center, it easily gives rise to stagnation of the catalytic cycle due to competitive adsorption. Bimetallic or multi-component synergistic systems achieve perfect "division of labor and collaboration" through decoupling in spatial and chemical functions. For example, one metal component is responsi-

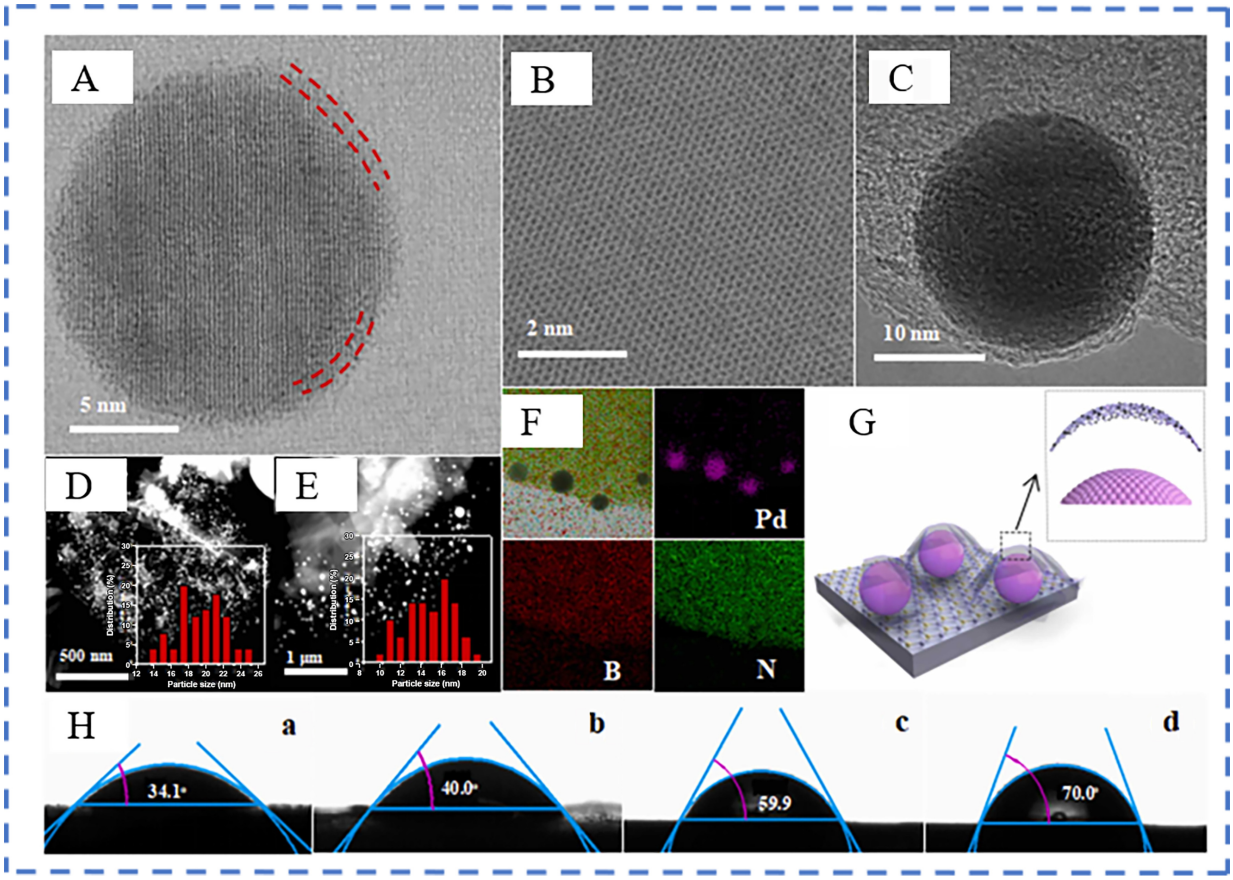

Figure 6. (A and B) Aberration-corrected HAADF-STEM images of Pd@NC/BN-2; (C-E) HAADF-STEM images of Pd@NC/BN-1 (D) and Pd@NC/BN-2 (C and E), the insets show the corresponding particle-size distributions; (F) EDX elemental mappings of Pd@NC/BN-2; (G) Schematic illustration of the array of different components in Pd@NC/BN; and (H) contact angle of the porous membrane on (a) Pd/Al_2O_3, (b) Pd/BN, (c) Pd@NC/BN-1, and (d) Pd@NC/BN-2[67]. This figure is quoted with permission[67]. Copyright 2022, Elsevier. HAADF-STEM: High-angle annular dark-field scanning transmission electron microscopy; EDX: energy-dispersive X-ray spectroscopy.

ble for preferentially capturing and activating VOC molecules with substantial steric hindrance, while the adjacent metal component serves as a "sacrificial site" or an oxygen supply hub, specifically responsible for accommodating water or accelerating the formation of active oxygen species [Figure 5C-F][61,62]. More interestingly, an appropriate amount of heterogeneous doping can even alter the action path of water, prompting interaction between adsorbed water and doped sites that convert into the highly active -OH species, which in turn assist in deeply tearing the C–C bonds of intermediate products (e.g., formates and acetates)[63]. This synergistic strategy not only mitigates water film formation via geometric dilution but also converts water from a reaction poison into co-catalytic species that facilitate VOC oxidation[64].

Modification of metal oxides

In supported catalyst systems, metal oxide supports have been frequently regarded as "inert platforms" for dispersing active components. Under humid working conditions, however, it is often the support surface that first comes into large-area contact and undergoes a strong interaction with water molecules[65].

Firstly, interfacial hydrophobic modification and thermodynamic repulsion effects constitute the first physical barrier blocking moisture intrusion[66-68]. By grafting inorganic siloxanes[69], introducing fluorine-containing ligands[70], or coating with low-surface-energy substances[71] (e.g., N-doped carbon[67]) on the metal oxide surface, the solid-liquid-gas three-phase contact angle can be effectively regulated, strictly limiting the enrichment of water clusters and capillary condensation at the interface on a spatial scale[66,72] [Figure 6][67]. The introduction of such superhydrophobic coatings or hydrophobic ligands thermodynamically constructs a hydropho-

bic (VOCs-preferential) differentiated partition microenvironment. The catalyst can not only maintain high intrinsic activation capability but also induce the interaction between gaseous oxygen and residual water molecules to generate additional active oxygen (e.g., *OOH and *OH) species, thereby suppressing water-induced blockage while compensating for lattice oxygen consumption[73,74].

Second, the reconstruction of surface acid-base properties and the inhibition of hydroxylation are the key to regulating water adsorption behaviors at the chemical bond level. The adsorption and deep dissociation of water molecules on oxide surfaces depend strongly on surface Lewis or Brønsted acid sites and strongly polar basic oxygen sites. If an excessive number of high-strength polar sites exist on the support surface, it easily induces the irreversible chemisorption of water, gradually developing into a dense surface hydroxyl layer[75-77]. Through rational heterogeneous element doping[78,79] (such as introducing specific non-metallic elements to replace surface hydroxyls) or constructing multi-component composite oxides[80], the local charge distribution can be effectively adjusted to placate the extreme acid-base potential of the support surface. The goal of this acid-base microenvironment optimization is not to absolutely eliminate the acid sites but to establish a more moderate adsorption balance, i.e., to ensure efficient capture of VOC molecules with specific functional groups while kinetically greatly increasing the energy barrier for water molecule dissociation to form stable hydroxyls, maintaining water molecules in a weakly adsorbed state that is easy to desorb[81].

Finally, strengthening lattice oxygen migration and the underlying compensation of the MvK mechanism are the core kinetic guarantees for maintaining high-humidity reaction continuity[82-86]. Most metal oxides catalyze VOC oxidation according to the MvK mechanism, and the most detrimental effect of moisture is cutting off the cycle channel for gas-phase oxygen activation and lattice-oxygen replenishment through hydroxyl coverage. To break through this limitation, designing composite supports (e.g., solid solutions like Ce-Ti[87], Cu-Mn[88], Cu-Co[89] or interfacial structures[90,91]) to induce strong lattice distortion can endow the support with an extremely strong oxygen storage capacity and excellent bulk oxygen mobility[21]. When water molecules inevitably mask part of the surface active sites, this type of modified support can act as an efficient lattice oxygen reservoir. It continuously delivers the highly active lattice oxygen and surface oxygen species to the active reaction interface through rapid oxygen transport from the bulk or subsurface[91]. Meanwhile, precisely constructed oxygen vacancies can not only promote O_2 activation but also suppress H_2O adsorption through the charge transfer effect[92]. This enables the support to favorably modulate the competitive equilibrium between moisture adsorption and active oxygen replenishment.

Regulation of support crystal phase and facet

In heterogeneous catalytic systems, the water-resistance performance of the catalysts depends not only on their macroscopic chemical compositions but also, at a deeper level, is controlled by the spatial arrangement of surface atoms. A large number of studies have demonstrated that even under the premise of identical chemical composition and overall defect concentration, differences in the primary exposed crystal planes of the support or transitions in the crystal phase can lead to poles apart in activity retention under humid working conditions[93].

Firstly, tailoring the surface coordination environment and reshaping intrinsic polarity are the most direct pathways by which crystal facet regulation influences water adsorption thermodynamics. Different crystal facets expose distinctly different metal/oxygen atom ratios, geometric configurations, and low-coordination states of surface atoms. These atomic-level geometric discrepancies directly translate into significant changes in surface free energy and local charge distribution. Using directional synthesis techniques to selectively expose specific crystal facets, the intrinsic polarity and hydrophilic/hydrophobic tendencies of the catalyst surface can be fundamentally altered[60,94]. For example, certain specific facets can widen the formation distance of the hydrogen bond network among water molecules through special atomic spacing, hence blocking the spreading of a dense water film at the molecular scale[95,96]. Meanwhile, the tailored local coordination environment can precisely weaken the binding energy between polar water molecules and surface sites, reversing the competitive adsorption disadvantage of H_2O against specific organic substrates (e.g., VOCs) at the thermodynamic level.

Secondly, the dynamic regeneration of active hydroxyl groups and the optimization of intermediate evolutionary pathways elucidate the promotional kinetic effect of moisture on specific crystal facets. Water molecules do not strictly function as the inhibitory species. On facets featuring step sites or specialized metal-support interfacial topology, the activation of water can be effectively harnessed to facilitate the reaction[97]. For example, under the synergistic action of a specific proportion of oxidized metals and step sites, the moderate water dissociation can avoid the formation of a passivation layer while continuously and dynamically regenerating the highly active surface hydroxyl species (e.g., the highly active metal-OH)[98]. These *in situ* generated hydroxyls not only compensate for the interfacial oxygen deficiency induced by moisture but also serve as key mediators of proton or electron transfer. This facilitates surface migration and oxidative cleavage of reaction intermediates (e.g., conversion of spectator formates to the active carboxylates) on the catalyst surface. By leveraging the topological characteristics of specific crystal facets, this mechanism successfully redefines the role of water molecules, shifting them from competitive inhibitors to kinetic promoters that accelerate the intermediate evolution.

MOFs and their derivatives and porous confined structures

The introduction of porous confined structures (e.g., MOFs) and their derivatives provides a dimension of mass transfer and local microenvironment regulation for enhancing the water resistance of catalytic systems[99].

Firstly, pore confinement effects and precise sieving of molecular diffusion pathways constitute the preceding physical barrier to blocking moisture intrusion. In non-porous or macroporous systems, moisture-induced deactivation often initiates even before the surface reaction occurs, for instance, by preferentially occupying pore mouths, blocking internal diffusion paths, and locally forming dense hydrogen bond networks[100]. By constructing sub-nanometer or nanometer-scale confined spaces with specific geometric sizes and topological morphologies, porous structures can rearrange the diffusion kinetic competition between H_2O and macromolecular VOCs at the molecular scale[36,101,102]. This spatial confinement not only restricts the free assembly of bulky water clusters through physical steric hindrance but also forces water molecules and VOCs to undergo staggered-peak or diverted diffusion through directional transport in nanosized pores, greatly reducing the local concentration of H_2O around the active sites.

Secondly, customizing pore-wall chemical properties and reshaping the local hydrophobic microenvironment strip water of its competitive advantage at the thermodynamic level. Whether in pristine MOF materials or their derivative structures, highly hydrophobic "microclimate zones" can be constructed on the inner pore walls through ligand modification or retention of carbon/heteroatoms during the derivation process [Figure 7A and B][103,104]. This hydrophobization within the confined space is not a simple surface coating but rather completely disrupts the tendency of water to form local hydrogen bond networks through dense non-polar groups or local electric fields on the pore walls. When reactant molecules penetrate this microenvironment layer, the hydrophobic pore walls exert a strong affinity and enrichment effect on non-polar or weakly polar VOC molecules, while thermodynamically repelling water molecules outside the core reaction zone, causing water to lose most of its competitive advantage before approaching the actual catalytic interface.

Finally, the topological inheritance and multi-center synergy of MOF derivatives endow the catalysts with multi-dimensional repair capabilities under hot and humid working conditions. To address the limitations of MOF-derived materials in terms of high-temperature thermal stability and water resistance, the incorporation of heterometals can significantly enhance the redox stability of the framework and the structural integrity of the derived oxide skeleton [Figure 7C and D][105]. Meanwhile, constructing MOF-carbonaceous/oxide composite systems can simultaneously build hydrophobic barriers and reinforce mechanical properties. Using MOFs as precursors for thermal or non-thermal derivation allows for inheriting their highly regular porous skeletons and *in situ* generating atomically dispersed heterogeneous metals (e.g., multimetallic alloyed nanoclusters[106] or metal oxides with high defect states[107,108]) within the confined space. This derivation not only overcomes the weak temperature resistance of pristine MOFs but also effectively prohibits water vapor-induced sintering and agglomeration of active components via the strong metal-framework interac-

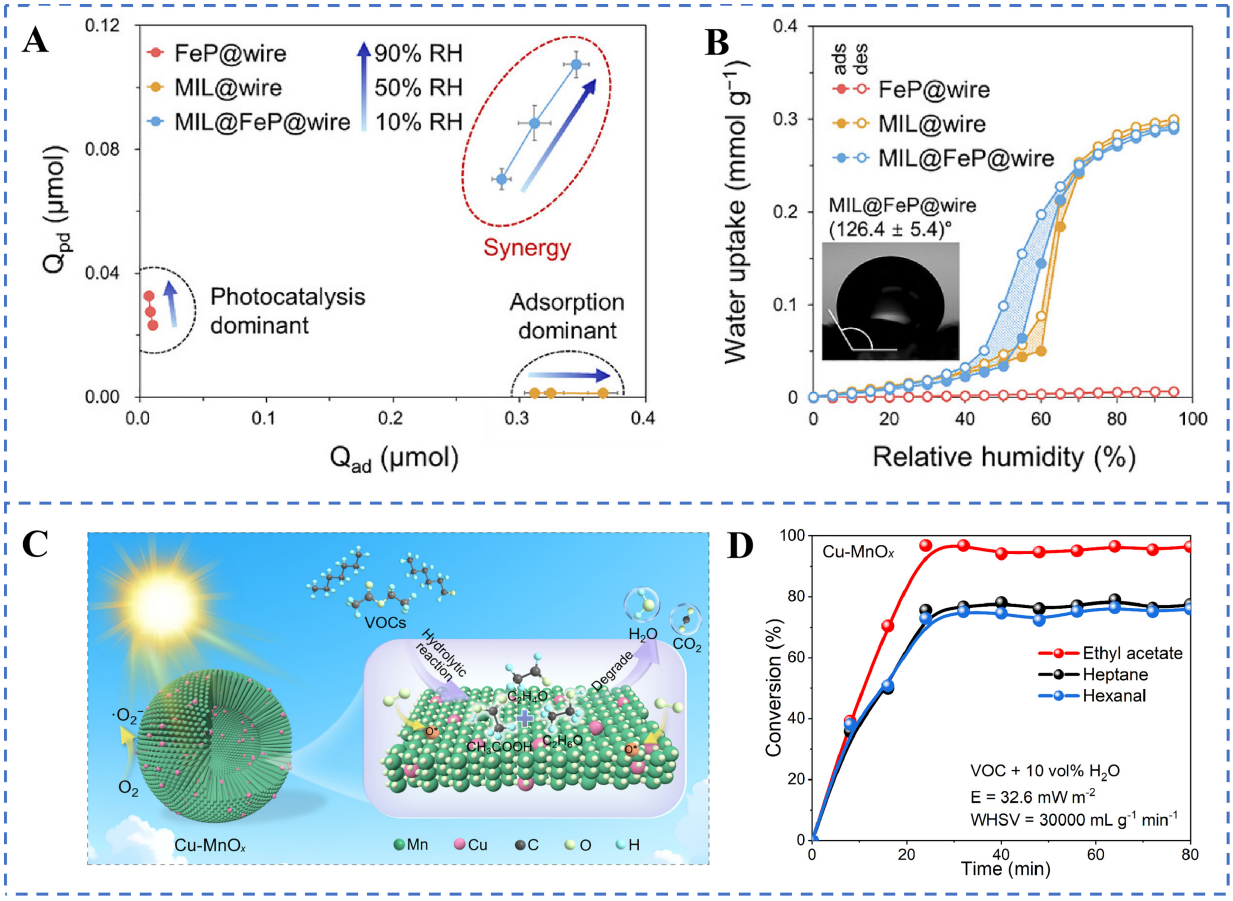

Figure 7. (A) Q_{ad} *vs.* Q_{pd} plot for C_6H_{12} vapor removal on FeP@wire, MIL@wire, and MIL@FeP@wire under different RH conditions; (B) Water vapor adsorption-desorption isotherms of FeP@wire, MIL@wire, and MIL@FeP@wire; the inset image shows the static water contact angle of MIL@FeP@wire[104]. (A and B) are reproduced from reference[104] under the Creative Commons CC BY License; (C) Schematic diagram of the main reaction pathways of three VOCs over the Cu-MnO_x catalyst; (D) Time-dependent catalytic conversion of ethyl acetate, heptane, and hexanal over the Cu-MnO_x catalyst under humid conditions. (In a flow reactor, 0.2 g catalyst, 100 mL·min^{-1}, 0.1 MPa, 30,000 mL·g^{-1}·h^{-1} of WHSV)[105]. (C and D) are reproduced from reference[105] under the Creative Commons CC BY License. VOCs: Volatile organic compounds; RH: relative humidity; WHSV: weight hourly space velocity.

tions and local confinement. More interestingly, in specific multimetallic derivative frameworks (e.g., transition metal and alkali metal synergistic systems), a moderate amount of moisture intruding into the pores, rather than giving rise to poisoning, can instead be activated by the specific sites and converted into reaction auxiliaries promoting the deep mineralization and tearing of VOCs (e.g., toluene)[109-112].

EXPLORATION OF MECHANISMS FOR EXTERNAL FIELD-ASSISTED ENHANCEMENT OF WATER RESISTANCE FOR CATALYTIC OXIDATION OF VOCS

Photo/Photothermal-assisted catalysis

In traditional thermal catalysis, the core issue underlying moisture inhibition lies in the strong bonding between polar water/hydroxyl species and active sites at low temperatures. Introducing a light field (ultraviolet, visible, or near-infrared light) not only expands the dimension of energy input but also fundamentally reshapes surface reaction kinetics through the photogenerated charge carriers or local thermal effects[113-116].

Photogenerated hole-mediated species transformation (pure photo-assisted mechanism)

In photocatalytic systems based on semiconductors (e.g., TiO_2, ZnO, g-C_3N_4, and their heterojunctions), the presence of a moderate amount of water vapor undergoes a nature reversal, becoming a key reactant promoting the deep mineralization of VOCs[117]. The microscopic physical mechanism is as follows: under excitation by photons of specific wavelengths,

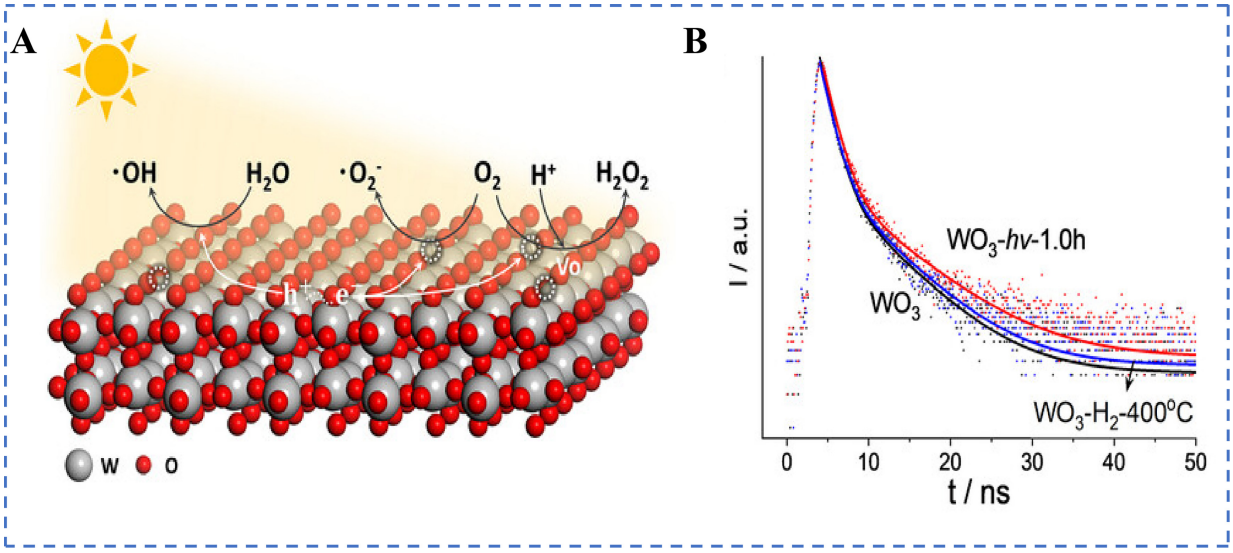

Figure 8. (A) Schematic illustration of O_2 and H_2O activation over WO_3-*hv*; (B) Time-resolved PL decay curves of WO_3, WO_3-*hv*-1.0 h, and WO_3-H_2-400 °C[118]. This figure is quoted with permission[118]. Copyright 2024, John Wiley and Sons. PL: Photoluminescence.

photogenerated holes (h^+) with an extremely high oxidation potential are generated in the semiconductor valence band. These high-energy holes can directly strip electrons from water or hydroxyls (-OH) preferentially adsorbed on the catalyst surface, initiating the reaction of $H_2O_{ads} + h^+ \rightarrow \cdot OH + H^+$, hence generating hydroxyl species (·OH) with an ultra-strong oxidizing ability.

Local hot spots and hot electron injection (photothermal synergistic mechanism)

In addition to pure photochemical reactions, the photothermal effect provides the "targeted energy" to overcome the water desorption energy barrier. Through non-radiative relaxation of photons by specific plasmonic metals or photothermal supports, light energy is converted into local hot spots, accompanied by the injection of high-energy hot electrons [Figure 8]. This targeted local transfer of energy effectively overcomes the kinetic energy barriers for water desorption and surface hydroxyl recombination, enabling the catalytic interface to maintain a dry state similar to high-temperature thermocatalysis even under macroscopic low temperatures, thus effectively solving the problem of active-site regeneration in humid environments[79,118-120].

Catalytic ozonation

In addition to introducing a light field, utilizing ozone (O_3) to replace or assist conventional O_2 is another potent "proactive regulation" water-resistance strategy. Conventional thermocatalysis is highly prone to catalyst deactivation by moisture, largely because water molecules poison the catalyst's electron-donor sites, hindering the dissociative activation of background O_2. O_3, as a high-energy-state oxidant, has an extremely low decomposition activation energy barrier on the catalyst surface, fundamentally circumventing the traditional high-energy barrier of oxygen activation steps[121-123]. In catalytic ozonation systems, the involvement of water molecules is no longer limited to simple competitive adsorption. Water can undergo strong coupling with primary oxygen species generated from O_3 decomposition, promoting the formation of a more reactive cascade of reactive oxygen species (ROS) radical network[124-126]. This mechanism perfectly transforms the role of water molecules from a "poisoning site-occupier" into a "promoter of radical chain reactions", achieving a fundamental leap in water-resistance performance[127,128].

Although thermal, photothermal, and O_3-assisted catalysis have each shown good potential for VOC removal under humid conditions, their synergistic integration has been rarely explored. In particular, the combined use of light and O_3 may further improve low-temperature catalytic activity and water tolerance, but several challenges remain, including (i) the mismatch between photogenerated

charge transfer and O_3 activation kinetics; (ii) excessive nonselective radical generation; (iii) catalyst over-oxidation or instability under simultaneous light and O_3 exposure; and (iv) the difficulty of simultaneously regulating water adsorption, O_3 activation, and VOC oxidation at the same interface. To overcome these limitations, future studies should focus on rational interfacial design, such as heterojunctions or defect-engineered interfaces for efficient charge separation, dual-functional active sites for selective O_3 activation and rapid hydroxyl removal, hydrophobic-reactive surfaces to suppress water accumulation, and plasmonic or photothermal structures to accelerate the desorption of water and intermediates.

CONCLUSION AND OUTLOOK

Despite significant progress in designing water-resistant catalysts and external field-assisted technologies, a gap remains between current research and practical industrial applications. To further promote the development of VOC purification technologies under high-humidity and complex working conditions, future research urgently needs to achieve breakthroughs in the following aspects:

(1) Breaking through the limitations of static characterization and deepening operando dynamic mechanism resolution. Under real reaction conditions, adsorption, water dissociation on the catalyst surface, and transient coupling with VOCs are highly dynamic and complex. In the future, there is an urgent need to develop and combine advanced operando characterization techniques, such as Operando DRIFTS, near-ambient pressure XPS (AP-XPS), and isotope tracing techniques, to capture the evolution of transient intermediates at the dynamic gas-solid interface. Combined with microkinetic modeling and artificial intelligence (AI)/machine learning-assisted molecular dynamics simulations, these approaches are expected to accurately depict the full panorama of the dynamic spatiotemporal evolution of water-VOC active sites at the atomic scale.

At the same time, to make AI-assisted screening more predictive and transferable, future studies should prioritize the establishment of unified water-catalyst interaction datasets under comparable reaction conditions. In particular, descriptor construction should focus on key physicochemical parameters that directly govern water adsorption, activation, and poisoning behavior, including water adsorption energy, water dissociation barrier, hydroxyl desorption energy, *d*-band center or other electronic-structure descriptors related to adsorbate interactions, oxygen vacancy formation energy and vacancy density, lattice oxygen mobility and reducibility, surface acid-base properties, and hydrophobicity-related parameters such as surface polarity or contact angle. In addition, structural descriptors, including coordination environment, exposed crystal facets, pore confinement effects, and metal-support interaction strength, should also be incorporated to better describe the complexity of practical catalyst systems. More importantly, descriptor selection should be continuously validated by combined experimental-computational workflows to build robust predictive models for the rapid screening and rational design of water-resistant catalysts.

(2) Facing real industrial scenarios directly and exploring the coupling effects of multi-dimensional complex working conditions. Most existing water-resistance assessments are based on ideal laboratory conditions (single VOC + pure water vapor). However, real industrial waste gases (such as painting, chemical, and pharmaceutical waste gases) are often mixtures of multi-component VOCs, accompanied by severely fluctuating humidity (relative humidity = 10%-90%), and may contain impurity gases [such as SO_2, NO_x, and halogens (e.g., HCl)]. Therefore, future studies should move beyond single-factor evaluation and establish a standardized testing protocol for long-term hydrothermal aging and resistance to multiple poisons. Such a protocol should specify the reaction temperature, water vapor partial pressure or relative humidity, aging duration, gas hourly space velocity, pollutant composition, and coexisting poisonous gas concentrations, so that the catalyst stability can be benchmarked under comparable conditions.

More importantly, normalized descriptors should be introduced to improve cross-study comparability, such as the activity retention ratio under humid conditions, dry-state recovery coefficient after water removal, irreversible deactivation fraction after hydrothermal aging, and durability index under specified water partial pressure and temperature. On this basis, the practical applicability of single-atom,

bimetallic, and MOF-derived catalysts can be quantitatively benchmarked in a more unified manner. In addition, catalyst design should evolve from single water-resistance optimization toward integrated multi-resistance regulation. In other words, future catalysts should simultaneously balance water tolerance with sulfur- and halogen-resistance without sacrificing VOC oxidation activity, through the rational regulation of hydrophobicity, acidity-basicity, oxygen mobility, defect chemistry, and metal-support interfacial stability. Only by introducing long-term, all-weather, and multi-poison evaluation criteria, the multi-resistance catalyst design can move from the proof-of-concept laboratory studies toward truly industrially relevant catalyst development.

(3) Bridging the nano-micro scale gap and advancing the engineering scale-up of structured reactors. The vast majority of the excellent water-resistance performance reported in the current literature is based on the mg-scale powder catalysts, which have huge macroscopic mass transfer differences compared to the shaped catalysts used industrially (e.g., honeycomb ceramics and metal wire mesh). Under actual high-humidity working conditions, water vapor is highly prone to capillary condensation within the mesoporous network of shaped catalysts, causing serious internal diffusion limitations. Future research should pay close attention to pore engineering and mass or heat transfer optimization of macroscopic structured catalysts, especially for the external field-assisted systems (e.g., the light penetration depth limitation of photothermocatalytic reactors and the fluid dynamics design of O_3 distribution), and achieve seamless transformation from "powder-level activity" to "device- or reactor-level efficiency".

DECLARATIONS

Acknowledgments

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Methodology: Deng, J.; Sun, W.
Writing - reviewing and editing conceptualization, methodology, supervision, project administration: Liu, Y.; Dai, H.

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Ethical approval and consent to participate

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Consent for publication

Not applicable.

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