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Perspective

Role of H_2O in Catalytic Conversion of C_1 Molecules

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ABSTRACT: Due to their role in controlling global climate change, the selective conversion of C_1 molecules such as CH_4, CO, and CO_2 has attracted widespread attention. Typically, H_2O competes with the reactant molecules to adsorb on the active sites and therefore inhibits the reaction or causes catalyst deactivation. However, H_2O can also participate in the catalytic conversion of C_1 molecules as a reactant or a promoter. Herein, we provide a perspective on recent progress in the mechanistic studies of H_2O-mediated conversion of C_1 molecules. We aim to provide an in-depth and systematic understanding of H_2O as a promoter, a proton-transfer agent, an oxidant, a direct source of hydrogen or oxygen, and its influence on the catalytic activity, selectivity, and stability. We also summarize strategies for modifying catalysts or catalytic microenvironments by chemical or physical means to optimize the positive effects and minimize the negative effects of H_2O on the reactions of C_1 molecules. Finally, we discuss challenges and opportunities in catalyst design, characterization techniques, and theoretical modeling of the H_2O-mediated catalytic conversion of C_1 molecules.

1. INTRODUCTION

Water (H_2O) is intimately related to numerous chemical reactions. In living organisms, almost all chemical reactions take place in aqueous medium. H_2O plays the role of solvent, reactant, byproduct, catalyst, and proton transfer agent. For a long time, the understanding of H_2O has been mainly limited to its role as a reaction medium, while knowledge of other functions of H_2O in chemical reactions is insufficient.[1,2] With the development of experimental detection techniques and advancements in computational chemistry, the structure and dynamics of H_2O molecules have been studied at the molecular level to investigate the multifaceted effects of water on chemical reactions.[3−6]

Apart from its well-known role as a solvent or an intentionally added component, the presence of H_2O is often unavoidable in other nonaqueous environments. For example, H_2O molecules may be present in reactants or products adsorbing on the surfaces of catalysts.[7,8] Its presence is frequently identified as a destructive factor that shortens the lifetime of catalysts, reduces the production of desired compounds, reacts with intermediates and products to cause side reactions, and influences the performance of working catalysts.[9−11] On the other hand, numerous cases have demonstrated that H_2O can play a role as a participant or promoter,[12−17] supply or stabilize highly reactive species,[18−20] create a microscale solvation environment,[21−23] and enhance reaction rates and product selectivity in heterogeneous catalysis. These effects are especially important for gaseous phase reactions, including a variety of transformations to upgrade C_1 molecules such as CH_4, CO, and CO_2 that can enable the production of value-added chemicals from inexpensive feedstocks.

The effects of H_2O in catalytic reactions have been highlighted in several recent Reviews and Perspective articles.[6,24] Resasco et al. provided a review on the H_2O-mediated heterogeneously catalyzed reactions of primarily large hydrocarbons and biomass-derived molecules.[25] Ma and co-workers focused on catalytic reactions that occur in the aqueous phase, including alcohol or biomass-derived polyol reforming, CH_4 activation, and other C_1 reactions.[26] The present article is devoted to providing a perspective on H_2O-mediated thermocatalytic conversion of gaseous C_1 molecules including CO_2, CO, and CH_4. Specifically, in this Perspective, we briefly review the state and function of H_2O in catalytic reactions involving C_1 molecules that occur mainly in the gaseous phase. We will then discuss the promoting effects of H_2O in these reactions and various methods to overcome the negative effects of H_2O. We will also discuss challenges and future opportunities in catalyst design, characterization techniques, and theoretical modeling of the H_2O-mediated catalysis of C_1 molecules.

2. H_2O AS A PROMOTOR OR COREACTANT IN CO REACTIONS

2.1. Water−Gas Shift Reaction. As one of the most important reactions to produce hydrogen in the energy and chemical industries, the water−gas shift (WGS) reaction ($CO + H_2O \rightarrow H_2 + CO_2$, $\Delta H^0 = -41$ kJ/mol) has been widely studied. In addition, the WGS reaction and its reverse reaction are directly or indirectly relevant to other catalytic systems relying on the coexistence of H_2O with CO, H_2, or CO_2,

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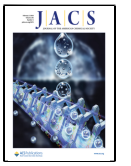

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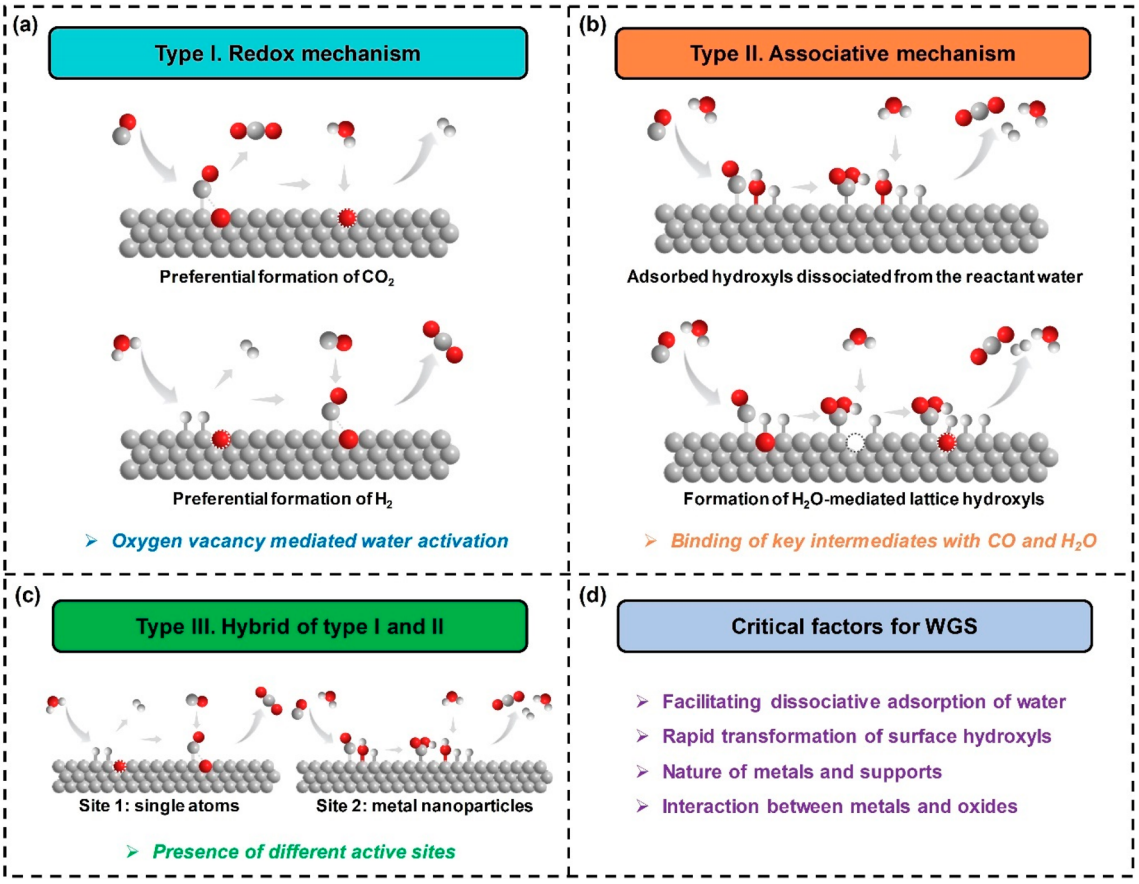

Figure 1. A summary of reaction mechanisms in the water−gas shift reaction. (a) Type I: redox mechanism. (b) Type II: associative mechanism. (c) Hybrid mechanism of types I and II. (d) Critical factors for the water−gas shift reaction.

including methanol synthesis, Fischer−Tropsch synthesis, methanol steam reforming, and coal gasification. Therefore, understanding the role of H_2O in the WGS reaction is also beneficial for clarifying the reaction mechanisms of the above-mentioned reactions.

Two types of reaction mechanisms are typically considered for the WGS reaction: the redox or regenerative mechanism and the associative mechanism (Figure 1).[27,28] For the redox mechanism, it has been proposed that an adsorbed CO molecule reacts with an activated oxygen atom from the catalyst to produce CO_2, generating an oxygen vacancy site. The reduced catalyst is then replenished by H_2O dissociation, leading to the formation of H_2. In the associative mechanism, adsorbed CO is consumed by reacting with OH from H_2O dissociation to generate carboxyl (COOH*) or formate (HCOO*) species as key intermediates. Though the precise mechanism is a matter of intense debate, both mechanisms involve a water dissociation step that is generally regarded as energetically important and, in some cases, as the rate-determining step (RDS).[27,29−31]

Regarding the redox mechanism (Figure 1a), one debate is focused on the reaction sequence of H_2O dissociation and CO conversion.[32] The oxygen species responsible for the conversion of surface-adsorbed CO to CO_2 can be derived from the surface lattice oxygen of the catalysts, and the subsequent oxygen vacancies provide active sites for H_2O dissociation, resulting in the formation of CO_2 before H_2.[33] In contrast, H_2O may first be activated on the catalyst surface to generate H_2 and reactive oxygen species, which then react with the adsorbed CO to form CO_2, resulting in the production of H_2 before CO_2.[34,35] Moreover, for supported metal catalysts, interfacial bifunctional sites ($M_1-O_v-M_2$) have also been proposed, in which CO is adsorbed on the metal site and H_2O undergoes dissociation on the oxygen vacancies of the oxide support, followed by the subsequent reaction between adsorbed CO and the dissociated species at the metal−oxide interface.[28,32,36,37]

It is reported that the dissociation of H_2O on a defective oxide surface is more thermodynamically preferred than on a well-defined oxide surface.[27,31] The nature of oxide supports (e.g., TiO_x, CeO_x, FeO_x and Al_2O_3), which strongly affect the presence of oxygen vacancies, plays an important role. A comparative study on Au/Al_2O_3 and Au/TiO_2 catalysts shows that H_2O bonds weakly at the $Au-Al_2O_3$ interface, while a much stronger binding for H_2O is observed on the Au/TiO_2 catalyst due to the presence of oxygen vacancies.[38] As a result, the reaction rate per total mole of Au for Au/TiO_2 is 20 times higher than that for Au/Al_2O_3. The reduced apparent activation energy of H_2O dissociation on Au/TiO_2 demonstrates that the oxide support is directly involved in the activation of H_2O.[38] In addition, an investigation on the Au@TiO_{2-x}/ZnO catalyst with a TiO_{2-x} overlayer on the surface of Au nanoparticles using *Quasi in situ* X-ray photoelectron spectroscopy (XPS), *in situ* extended Xray absorption fine structure (EXAFS), and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) confirms that both the electron-enriched $Au^{\delta-}$ species and oxygen vacancies directly participate in the dissociation of H_2O.[39] Similar

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observations have also been reported on Ni/TiO_{2-x}, Au/CeO_{2-x}, and Ir/FeO_x catalysts.[31,35,36]

In the case of the associative mechanism (Figure 1b), the hydroxyl groups from the dissociation of H_2O play an important role.[40] The OH species originating from H_2O alter the adsorption or readsorption behavior of reactants or products, leading to significant differences in the WGS activity and selectivity. Results from theoretical calculations indicate that wetting of the catalyst is controlled by the presence of OH groups on the surface, acting as anchors for water adsorption.[41] Moreover, favorable hydrogen bonding interactions stabilize the Zundel cations ($H_5O_2^+$) adsorbed on metal clusters and weaken the O−H bonds of adsorbed H_2O, thereby exhibiting a lower energy pathway for H_2O dissociation.[34] In addition to influencing the adsorption step, the OH species can also participate by reacting with CO to form carboxyl or formate intermediates. By comparing a density functional theory (DFT)-based microkinetic model with experimental reaction rates, Gokhale et al.[30] reported that the dissociative adsorption of H_2O is the RDS for the WGS reaction on the Cu(111) surface. Compared with formate, which tends to block active sites, carboxyl is a more reactive intermediate. It reacts with an adjacent OH group on the Cu(111) surface, forming CO_2 and H_2O (COOH* + OH* → CO_2* + H_2O*). Therefore, H_2O in the WGS reaction not only reacts with CO to form CO_2 and H_2 but also acts as a promoter to facilitate the reaction due to the formation of adsorbed OH* groups.[30] Likewise, by using *in situ* DRIFTS, Fu et al.[31] reported that the bridging-OH groups formed on the surface oxygen vacancies of the CeO_2 support are the key reactive species for the WGS reaction on Au-CeO_2 catalysts. The abundant Au-CeO_2 interfacial sites effectively promote the reaction between adsorbed CO on Au and bridging-OH groups formed on CeO_2. For larger Au nanoparticles supported on CeO_2, the limited number of interfacial sites leads to insufficient CO adsorption and thus weaker reactivity with the bridging-OH groups.[31] It is also proposed that there is a competitive adsorption of CO_2 and H_2O on the surface of the catalysts, and the accumulation of surface carbonates blocks the active sites.[42] A facile reaction between the hydroxyl groups and the carbonate layer on the catalyst surface can prevent carbonate species from blocking the active sites.[42]

Similarly, preadsorbed H_2O or cofed H_2O can readily form surface hydroxyls on carbide catalysts.[40,43,44] For example, Ma and co-workers reported Au/α-MoC catalysts for low-temperature WGS reaction, where the α-MoC support facilitates the epitaxial growth of Au layers with altered electronic structures, which facilitate bonding with CO.[44] At a temperature of 303 K, H_2O is activated on α-MoC, and CO adsorbed on adjacent Au sites readily reacts with surface hydroxyl groups formed by H_2O decomposition.[44] However, when the adsorbed hydroxyl species cannot be promptly converted, there is a problem of deep oxidation of α-MoC during long-term catalytic processes, leading to catalyst deactivation. By adding Pt clusters and Pt single atoms, the excess surface active oxygen species can be eliminated, enhancing the stability toward WGS.[43]

It should be highlighted that the WGS reaction may occur simultaneously via both the redox mechanism and the associative mechanism, and the dominant pathway relies on the ability of the catalysts to facilitate H_2O dissociation (Figure 1c). Chen et al.[45] compare the activity of Pt/FeO_x catalysts with exclusively either Pt nanoparticles or single atoms for the WGS reaction and find that Pt nanoparticles accomplish the WGS process through an associative mechanism, with CO strongly adsorbing on the Pt nanoparticle sites and reacting with the OH* species generated by activation of H_2O on the FeO_x sites to form the formate intermediate. In contrast, Pt single atoms promote the formation of oxygen vacancies on FeO_x that dissociate H_2O to H_2 and adsorbed O, which then combines with the weakly adsorbed CO on the Pt sites to produce CO_2.

In summary, regardless of the reaction pathways, fundamental factors controlling water dissociation and subsequent conversion are closely related to the geometric and electronic structures of the oxide supports and metal components in WGS catalysts.[37] Strong interactions between the metal species and the support may promote the formation of unique interfacial sites for optimizing the catalytic performance for the WGS reaction.[36,39,46,47]

2.2. CO Oxidation. Due to the limited activities of the current WGS catalysts in commercial processes, approximately 0.5−1.0 vol % of unconverted CO remains in the H_2 stream, which can poison the catalysts in their subsequent utilization in hydrogen fuel cells or ammonia synthesis. Therefore, preferential oxidation of CO in the H_2-rich stream with the presence of H_2O plays an important role in the H_2 purification step for various applications.[48] Similar to the WGS reaction, the presence of H_2O in the feed gases modifies the catalytic activity for the CO oxidation reaction.[12]

Using a commercial Au/Al_2O_3 catalyst as an example, Saavedra et al.[49] reported that the selectivity of CO oxidation in the presence of H_2 can be optimized by controlling the coverage of water on the catalyst surface. Generally, preferential CO oxidation (PROX) selectivity increases with the partial pressure of water since H_2O has a more significant effect on blocking the sites for hydrogen adsorption than those for CO adsorption. As a result, with increasing H_2O partial pressure, the H_2 oxidation is inhibited, and a higher selectivity of CO oxidation is observed when the catalyst surface is covered by one to two monolayers of water. However, a further increase in the water partial pressure typically leads to the deactivation of the catalyst.

In addition to the PROX for H_2 purification, the role of H_2O in low temperature CO oxidation for emissions control has been extensively studied.[15,50,51] Depending on the catalyst used, H_2O can be either an inhibitor or a promoter. For noble metal catalysts, a trace amount of H_2O in the reactant feed stream is found to improve the CO oxidation activity by up to several orders of magnitude.[51−53] Many mechanistic questions regarding the role of H_2O in the CO oxidation reaction have been raised in the past two decades, which include: (i) whether gaseous H_2O directly participates in the formation of CO_2; (ii) whether the reaction occurs through the Mars−van-Krevelen (MvK) or the Langmuir−Hinshelwood (LH) mechanism; and (iii) whether the reaction pathways involve intermediates such as carboxyl, carbonate, or bicarbonate.[54−63]

For example, the catalytic activity of Au/TiO_2 under H_2O concentrations of 3−10 ppm has been observed to be about 10 times higher than under a dry condition (0.1 ppm). The reaction rate further increases with rising H_2O concentration, reaching a maximum at 200 ppm.[52] On the other hand, the presence of excessive H_2O can cover the active center of the catalyst, leading to a decrease in catalytic efficiency.[52,64] It has also been found that the influence of H_2O on the activity of Au catalysts strongly depends on the type of oxide (CeO_2, Fe_2O_3, TiO_2, Al_2O_3, SiO_2).[49,53,59,65−69] As shown in Figure 2a,b, Al_2O_3

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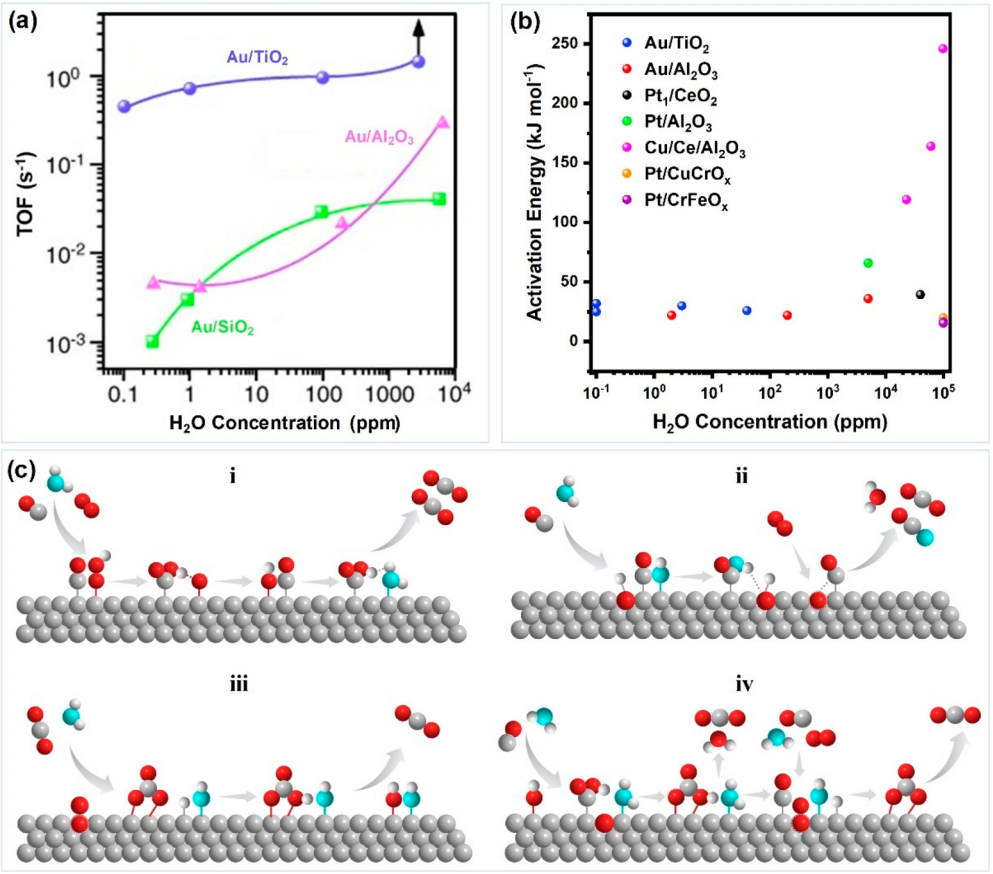

Figure 2. (a) Turnover frequencies (TOF) per surface gold atom at 273 K for CO oxidation over Au/TiO_2, Au/Al_2O_3, and Au/SiO_2 as a function of H_2O concentration. Upright arrow indicates the saturation of the CO conversion. Reproduced with permission from ref 53. Copyright 2004 Wiley. (b) A comparison of activation energy of CO oxidation catalysts in the presence of H_2O. Data originated from refs 52, 53, 61, 64, 70, 71. (c) Proposed reaction mechanism of the CO oxidation in the presence of H_2O.

seems more sensitive to the concentration of H_2O than others, while the apparent activation energy of CO oxidation appears to have little correlation with H_2O concentration for noble metal catalysts supported on other oxides.[52,53,61,64,70,71]

In general, it is accepted that the amount of H_2O adsorbed on the catalyst, rather than the H_2O concentration in the reactant feed, affects the activity.[52−54] Some H_2O-derived species on the catalyst surface are speculated to activate molecular oxygen and promote the dissociation of carbonate to avoid deactivation.[20,72−74] In the absence of H_2O, CO oxidation requires three steps: $CO + O_2 \rightarrow$ *cis*-OCOO* $\rightarrow$ *trans*-OCOO* $\rightarrow CO_2 + O^*$. The adsorption of trace amounts of H_2O near the active sites can facilitate the activation of oxygen, which is considered to be one of the RDS in CO oxidation. Saavedra et al.[18,68] have systematically investigated the mechanism of CO oxidation in the presence of H_2O over TiO_2 or Al_2O_3-supported Au catalysts using Infrared (IR) spectroscopy, kinetic experiments, and DFT calculations (Figure 2c-i). The weakly adsorbed H_2O on the catalyst surface increases the effective number of active centers without changing the intrinsic reactivity, and the coverage of H_2O largely determines the catalytic activity.[68] For H_2O-mediated O_2 activation, the barrier for O−O bond scission is reduced by 0.4 eV due to the formation of OOH* via proton transfer, which helps activate O_2 at low temperatures.[62] The interaction of CO* with OOH* to generate COOH* is more favorable than the interaction between CO* and surface OH*.[18] Therefore, weakly adsorbed H_2O is the key proton (H*) donor. In these studies, neither the H_2O nor the lattice oxygen of the oxide support is directly involved in CO_2 production at low temperatures on either reducible or inert oxides, and the rate enhancement mainly follows the H_2O-mediated LH reaction mechanism.

Carbonate accumulation on the catalyst surface can also lead to a decrease in CO oxidation performance due to the blockage of active sites by carbonate.[56] Further conversion of carbonate to bicarbonate can be promoted by proton transfer through an H-bonded H_2O network at the catalyst surface (Figure 2c-iii), which significantly reduces the activation barrier for CO_2 desorption from 1.5 to 0.6 eV.[62] A mechanism involving the presence of carbonate/bicarbonate intermediates and surface hydroxyl groups that enhance the rate has been proposed (Figure 2c-iv).[56] Specifically, surface hydroxyl groups drive the formation of carboxyl groups from CO, which are oxidized to bicarbonate by surface lattice oxygen and then decomposed to CO_2 and H_2O by reacting with H atoms produced from H_2O dissociation.

On the other hand, H_2O has also been proposed to play a promotional role by directly participating in the CO oxidation at low temperature (77 K).[57,58] The formation of hydroxyl groups through oxygen activation by H* produced from H_2O and its reaction with adsorbed CO to form CO_2 has been observed using an ultrahigh vacuum (UHV) scattering/analysis chamber and DFT calculations, which is similar to the results

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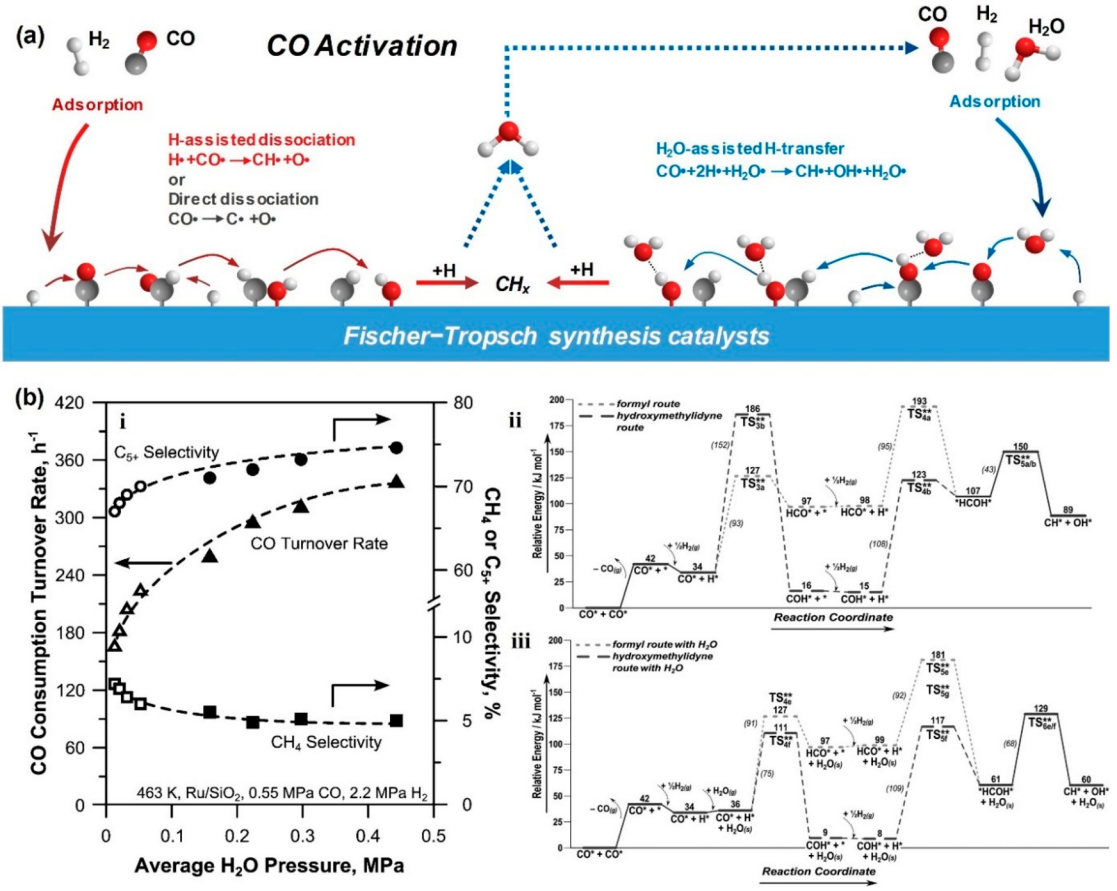

Figure 3. (a) Different mechanisms of CO activation on FTS catalysts. (b) Mechanistic role of H_2O on the rate and selectivity of FTS on Ru catalysts: (i) CO consumption rate (Δ or ▲), CH_4 selectivity (□ or ■), and C_{5+} selectivity (○ or ●) as a function of H_2O partial pressure on 5 wt % Ru/SiO_2 with a feed gas of H_2/CO = 4.5. Open symbols: conversion changes; closed symbols: H_2O addition; reaction coordinate diagrams for (ii) H-assisted CO activation via the formyl and hydroxymethylidyne routes in absence of H_2O, (iii) H_2O-mediated formyl and hydroxymethylidyne routes in the presence of H_2O. Reproduced with permission from ref 89. Copyright 2013 Wiley.

using single-atom catalysts.[71] Specifically, the hydroxyl groups from dissociated H_2O on the single atom Pt_1/CeO_2 catalyst react with adsorbed CO to form a highly reactive carboxyl intermediate, which is dehydrogenated with the assistance of hydroxyl groups to generate CO_2 and H_2O (Figure 2c-ii).[61] Such a pathway is more facile than the direct reaction of CO with the lattice oxygen, resulting in higher activity for CO oxidation.[61] On the other hand, Zhao et al. find that CeO_2-supported single Au atoms are more effective as an electron acceptor, offering a more efficient channel for the CO + OH reaction pathway in the presence of OH groups from water dissociation.[75]

2.3. Fischer–Tropsch Synthesis. Fischer–Tropsch synthesis (FTS) is another important catalytic reaction in industry that converts syngas (a mixture of CO and H_2) to value-added chemicals (hydrocarbons, oxygenates, etc.). The FTS reaction can be catalyzed using Fe-, Co-, and Ru-based materials.[76−78] H_2O is an inherent byproduct in FTS as one H_2O molecule is generated for each molecule of CO that is converted. H_2O produced or cofed with the syngas reactants has a significant effect (either positive or negative) on the reaction rate, hydrocarbon selectivity, FTS product distribution, and catalyst longevity due to its influence on the degree of syngas adsorption on the catalyst, chain initiation, chain growth, methanation, hydrogenation to paraffins, and dehydrogenation to olefins.[79]

Early studies have reported that the influence of H_2O is positive on unsupported and SiO_2-supported cobalt oxide catalysts, negative for Al_2O_3-supported catalysts, and slightly beneficial for TiO_2-supported catalysts.[79−82] These different H_2O effects are attributed to three aspects: oxidation of the Co catalyst, removal of transport restrictions via the formation of an H_2O-rich intrapellet liquid, and kinetic effects. Several mechanistic explanations have been offered to explain the influence of H_2O in FTS. One hypothesis is that higher H_2O partial pressure suppresses hydrogenation reactions at the surface by occupying sites for H_2 dissociation.[83] For Co/SiO_2 catalysts, increased reaction rates are due to the influence of H_2O on the active species distribution on the Co surface,[80] and adsorbed H_2O accelerates the CO dissociation rate with subsequent formation of CH_x monomers.[84,85] Coadsorbed H_2O presumably interacts with CO and lowers the energy barrier for CO activation. An increase in C_{5+} products is associated with an increased coverage of reactive monomer species due to an increased polymerization rate without a simultaneous effect on termination probability. Fischer et al.[86] have proposed the possibility of H_2O-induced changes on the active sites responsible for chain growth, or an inhibiting effect of H_2O on methanation sites. H_2O increases the amount of active surface carbon, which is present predominantly as a monomeric species. This increased surface concentration of monomeric carbon is caused by an acceleration of the CO

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dissociation rate without a corresponding activity increase of the downstream hydrocarbon synthesis steps.[83,87] Therefore, the proposed monomer dependencies in the FTS mechanism explain the lower methane selectivity and higher molecular weight products observed at increased H_2O concentrations.[84,88]

H-assisted pathways in kinetically relevant CO dissociation steps have also been proposed on both Fe and Co catalysts.[90] In such pathways, chemisorbed H* and CO* react to produce CH_xO species, which dissociate to form OH*. This leads to the preferential rejection of the O atoms in CO to produce H_2O. These assisted pathways are the exclusive CO activation routes on Co catalysts and the predominant ones on Fe catalysts. They happen concurrently with unassisted CO dissociation on Fe-based catalysts, wherein rejected oxygen leaves are treated as CO_2 (Figure 3a).

Compared to Co-based catalysts, the effect of H_2O on the performance of Fe-based FTS catalysts is more complicated due to the simultaneous occurrence of the WGS reaction, which is less significant on Co-based catalysts.[91] The WGS reaction consumes CO along with H_2O produced during the FTS reaction to generate CO_2 and additional H_2. Therefore, for Fe-based catalysts, the addition of H_2O to the syngas feed affects the partial pressure of CO and H_2 inside the reactor by increasing the WGS rate. Karn et al.[92] reported that the presence of 10−30% H_2O in syngas with a 1:1 H_2/CO ratio does not significantly influence the CO conversion using a fixed bed reactor. In contrast, Satterfield et al.[93] proposed that cofeeding H_2O accelerates the deactivation of Fe-based catalysts in slurry-phase FTS when the H_2/CO ratio is 0.96. However, in the case of a H_2/CO ratio of 0.52, the cofeeding of 20% H_2O exhibits no influence on the FTS reaction rate. These studies show that the different roles of H_2O can be attributed to the difference in reactor type, amount of H_2O, H_2/CO ratio, and catalysts used.[94]

Similar to the case for the Co-based catalysts, a promotional role of water has been observed for FTS on Ru catalysts. Hibbitts et al.[89] have shown that with increasing H_2O pressure, the CO consumption rate and C_{5+} selectivity increase continuously, whereas the CH_4 selectivity decreases, as shown in Figure 3b-i. H_2O can significantly reduce the energy barrier of H-assisted C−O dissociation by facilitating H-transfer (Figure 3a, right). From DFT calculations, in the absence of H_2O, the kinetically relevant H-transfer step is the formation of the *HCOH* intermediate, which follows the formation of HCO* (formyl route). In this case, the barrier for HCO* formation is lower than that for *HCOH* formation (see Figure 3b-ii), resulting in a first-order H_2 dependence, which is in good agreement with experimental kinetic measurements. In contrast, in the presence of H_2O, the barrier for the H_2O-mediated path via the COH* (hydroxymethylidyne route) is lower than its counterpart in the formyl route (Figure 3b-iii). This reduced energy barrier accelerates the formation of activated C_1 species on the surface and, consequently, the overall rate.

In addition to theoretical simulations, recent development of *in situ/operando* characterization techniques enables a fundamental understanding of the catalytic process under real working conditions at different scales. For example, using magnetic resonance imaging (MRI), Zheng et al.[95] reported the distribution of liquid products and water molecules during FTS on a Ru/TiO_2 catalyst in a pilot fixed-bed reactor. Spatially resolved maps show that the product distribution becomes broad with a decreasing H_2/CO feed ratio. The observation of a higher concentration of heavier hydrocarbon chains within the catalyst pores than in the product wax confirms the effect of mass transfer on the overall catalytic process. Furthermore, *operando* two-dimensional MRI spectroscopy indicates that H_2O in the reactor accumulates on the surface of the pores of the catalyst, forming a water-rich local environment that influences the catalytic performance. Recently, Xu et al.[96] reported the enhanced selectivity toward liquid hydrocarbons in FTS on a bifunctional catalyst composed of a hydrophobic Fe-based catalyst and HZSM-5 zeolite. Molecular dynamic simulations coupled with experiments indicate different diffusion behaviors of H_2O on the catalyst surfaces with different hydrophilicity/hydrophobicity. On the hydrophilic catalyst, H_2O can easily reach the iron species encapsulated by the hydrophilic SiO_2 shell, leading to the WGS reaction. In contrast, after hydrophobic functionalization, the hydrophobic SiO_2 shell slows this process and thus prevents the WGS reaction on the Fe surface. As a result, a lower CO_2 selectivity is obtained on the hydrophobically functionalized catalyst with enhanced stability. These results demonstrate that by tuning the surface hydrophilicity/hydrophobicity different structures of H_2O molecules on the catalyst surface can be achieved to significantly influence the catalytic performance.

On the other hand, the metal-oxide particles can be modified by hydrophobic polymers such as polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE) to obtain hydrophobic materials.[97,98] It has been observed that the catalytic activity of a CoMnC/PDVB catalyst in FTS depends on the manner of mixing of the CoMnC and PDVB components.[99] Compared with a granule mixture (40 to 60 mesh), a powder mixture of the CoMnC and PDVB shows the highest CO conversion of 63.5% and C_2−C_4 olefin selectivity of 71.4%. The physical mixture of PDVB with CoMnC can modulate the local environment of the catalyst to rapidly remove the H_2O produced in syngas conversion and shift the H_2O-adsorption equilibrium on the catalyst surface.[100] Besides introducing hydrophobic substances to change the microenvironment of the active sites on the catalysts, the construction of a hydrophobic shell or functionalization of the catalyst surface with hydrophobicity is also an effective way to suppress side reactions involving H_2O.[10] For example, the presence of a hydrophobic SiO_2 surface layer in the core−shell FeMn@Si catalyst results in a decrease of the CO_2 selectivity from 45% on the traditional catalyst to about 13%, which is beneficial for the reduction of carbon emissions in FTS.

3. H_2O AS A BYPRODUCT OR PROMOTOR IN HYDROGENATION OF CO_2

H_2O is a byproduct in both the direct hydrogenation of CO_2 to methanol ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) and the main side reaction (reverse water−gas shift reaction: $CO_2 + H_2 \rightarrow CO + H_2O$).[101,102] In some cases, a small amount of H_2O may also be added to the feed gas as a promoter for methanol synthesis. Both positive and negative effects of H_2O, either as byproduct or additional feed, on methanol synthesis have been observed, which mainly depend on the nature of the catalysts and the partial pressure of H_2O. From the perspective of reaction mechanisms, some studies have shown that the H_2O byproduct might be involved in the reaction through H-transfer, or even participate as an H-source in methanol formation from CO_2 hydrogenation.[7,21,22,103]

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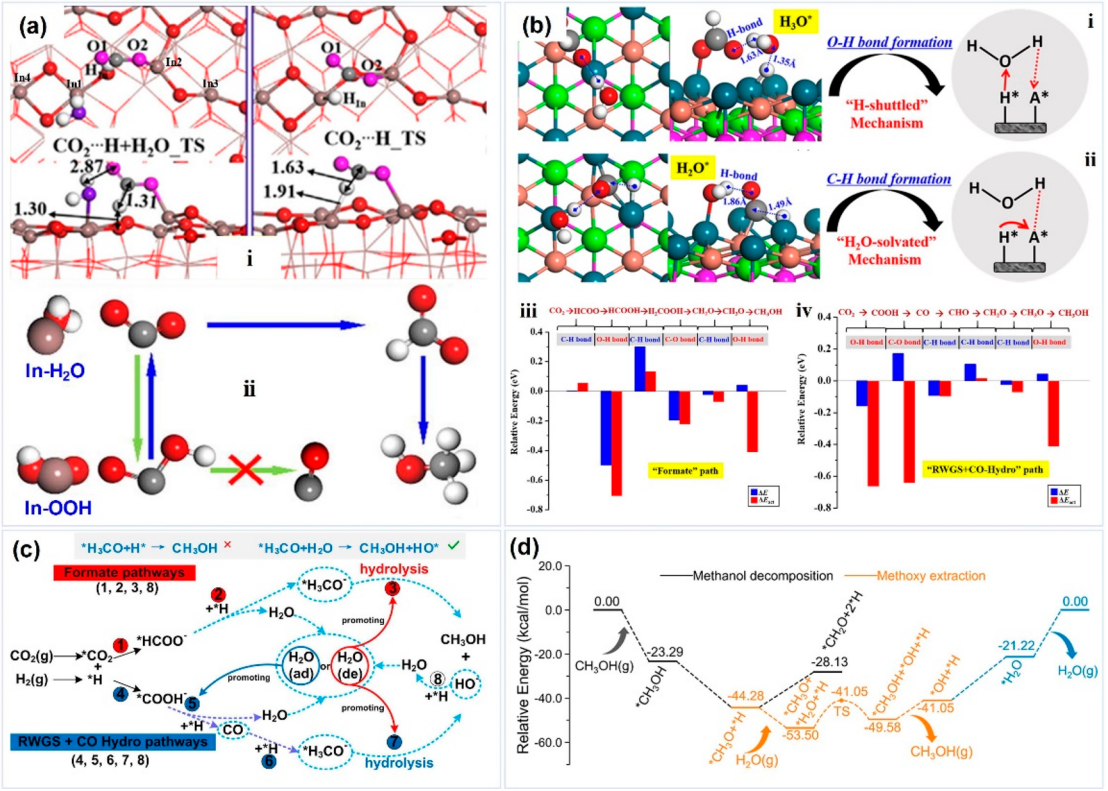

Figure 4. (a) Effect of adding H_2O to the feed gas over In_2O_3/ZrO_2 catalysts for CO_2 hydrogenation to methanol: (i) transition state (TS) configurations for HCOO* formation on an oxygen-defective $In_2O_3(110)$ surface in the presence and absence of H_2O; (ii) schematic illustration of the formation of InOOH species due to H_2O addition correlating with H_2O-dependent enhancement of CH_3OH formation. Reproduced with permission from ref 110. Copyright 2020 Elsevier. (b) Transition state configurations of (i) HCOO* → HCOOH* and (ii) CO* → CHO* steps involved in CH_3OH formation with H_2O included, from which the two "H-transfer" mechanisms are shown for the O−H and C−H bond formation reactions on PdCu(111). Effect of H_2O on reaction energetics for each elementary step in the (iii) "formate" and (iv) "RWGS+CO-Hydro" paths. ΔE represents the difference in reaction energy between the elementary step with H_2O and that without H_2O, and ΔE_{act} is defined in the same way but for the activation barrier. Reproduced with permission from ref 21. Copyright 2018 American Chemical Society. (c) Possible pathways of hydrogenation of CO_2 to methanol involving methoxy hydrolysis over Cu-ZnO-ZrO_2 catalysts. Reproduced with permission from ref 7. Copyright 2020 Elsevier. (d) DFT-calculated potential energy diagram for CH_3OH decomposition and methoxy extraction by H_2O on a Zr_3O_{10}/Cu(111) model surface. Reproduced with permission from ref 112. Copyright 2022 American Chemical Society.

It is generally accepted that CO_2 hydrogenation includes a pathway with a sequence of reactions involving adsorbed H, and direct hydrogenation with adsorbed H species alone is able to accomplish the production of methanol.[102,104] However, Yang et al.[105] observe via hydrogen titration that the direct hydrogenation of formate species involving adsorbed H species alone fails to produce significant quantities of methanol over Cu-based catalysts. They further propose that coadsorbates related to surface oxygen or H_2O-derived species may be critical to methanol production on Cu. In addition, a DFT investigation shows evidence for H_2O being involved in the CO_2 hydrogenation process via the H-transfer mechanism, where weakly bonded CO_2 is hydrogenated by one of the H atoms in H_2O, which facilitates the formation of the *trans*-COOH intermediate that is the RDS in the hydrocarboxyl mechanism.[22] The presence of H_2O can kinetically enhance the formation of the COOH* intermediate while formate hydrogenation is negligible or suppressed.[106] Similarly, a theoretical study over the $PdCu_3(111)$ surface shows that the coadsorption of H_2O not only enhances the adsorption of intermediates involved in the RDS but also lowers the activation barrier with the hydrogenation pathway following CO_2* → *trans*-COOH* → *t,t*-COHOH* → *t,c*-COHOH* → *c,c*-COHOH* → COH* → HCOH* → H_2COH* → H_3COH*.[107] In addition, the energy barrier of CO_2 hydrogenation to methanol can be reduced through the addition of a suitable amount of H_2O due to the enhanced conversion of the relatively stable intermediates of COOH* and CH_2O*.[108]

In the case of In-based catalysts, formate is considered to be a key intermediate in the hydrogenation of CO_2 to methanol, and the reaction mechanism can be understood as a hydride-proton transfer mechanism.[109,110] In the initial step of HCOO* formation, one H_2O molecule is placed on the In_1 site coadsorbed with a hydrogen atom (Figure 4a-i).[110] In the presence of H_2O, H* interacts with surface O to form OOH* due to spatial and electronic effects, which reacts with CO_2 to produce the C−H bond (Figure 4a-ii). While H_2O does not participate in the H-transfer process, the hydrogenation barrier is reduced by about 31% due to the presence of H_2O. Consequently, the presence of 0.1 mol % H_2O can reduce the activation barrier of the RDS (H_2COO* + H* ↔ H_2CO* + OH*) in the formate route, resulting in an increased CH_3OH yield of approximately 24%.

Nie et al.[21] systematically investigate the effect of trace H_2O coadsorption on each of the major "formate" and "RWGS +CO-hydro" methanol synthesis pathways, and also explore the chemical processes involved in C−O or C−H bond breaking, O−H bond formation, and C−H bond formation

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during methanol production (Figure 4b-i,ii). According to the different H-transfer and intermediate binding pathways, H_2O participation in the H-transfer mechanism is divided into a H-shuttle mechanism and an H-solvation mechanism. The former occurs through surface H* being transferred to the H_2O molecule, which simultaneously transfers another H to the adsorbed reaction intermediates to complete the hydrogenation. H_2O molecules do not need to be adsorbed to the surface, but can be present in the gas phase to stabilize intermediates through hydrogen bonding, e.g., O−H formation and C−O(H) bond breaking, $CO_2 \rightarrow COOH^*$, $COOH^* \rightarrow CO^* + OH^*$. The latter mechanism occurs through the adsorption of H_2O molecules by solvation of the nearby adsorbate, and hydrogenation proceeds via the direct transfer of surface H* to the adsorbate. The "H_2O-solvation" mechanism applies to all C−H bond formation reactions, such as $CO^* \rightarrow CHO^*$, where H_2O molecules are adsorbed onto the catalyst surface and undergo solvation by hydrogen bonding to the nearby adsorbate. The results of the effect of H_2O on the kinetic potential of the CO_2 hydrogenation show that in the formate pathway, the H_2O shuttle mechanism decreases the activation energy barriers for O−H bond formation ($HCOO^* \rightarrow HCOOH^*$, $CH_3O^* \rightarrow CH_3OH^*$) and C−O(H) bond breaking ($H_2COOH^* \rightarrow CH_2O^*$), while it has little effect on the C−H bond formation step (Figure 4b-iii,iv). H_2O exhibits a similar phenomenon for several basic steps of the "RWGS+CO-hydro" pathway. It should be emphasized that the selectivity obtained is based on DFT calculations, where the calculated energy potential is typically subject to an error of 0.2 eV. Therefore, it may be more appropriate to state that the two main routes are equally important for the hydrogenation of CO_2 to methanol.

On Cu-based catalysts, the direct hydrogenation of CH_3O^* exhibits a relatively high barrier, while H_2O as the hydrogen source can reduce the hydrogenation barrier to almost zero.[111] The presence of H_2O results in a reduction of the kinetic barriers of the elementary reactions. Further, our previous results over Cu-ZnO-ZrO_2 catalysts indicate that H_2O produced during CO_2 hydrogenation is a key active species, which tends to hydrolyze methoxy to methanol (Figure 4c).[7] An interconnected 3D ordered macroporous (3DOM) structure can effectively promote the desorption and diffusion of H_2O among catalyst particles, resulting in high methanol selectivity. Recent theoretical research supports the above findings and highlights that H_2O plays two important roles in the evolution of methoxy during CO_2 hydrogenation over the ZrO_2/Cu(111) surface: (i) preventing decomposition of methoxy and formation of methane by reducing the energy barrier of methoxy hydrogenation to methanol and (ii) extracting the adsorbed methoxy to form gaseous methanol (Figure 4d).[112]

An autocatalytic behavior of H_2O dissociation leading to the formation of its derivatives has also been reported.[113] Under near ambient conditions, H_2O−OH is the final state, wherein strong hydrogen bonding reduces the energy barrier of H_2O dissociation. Xu et al.[114] observe that the value of TOF_{CH_3OH} in the presence of surface O* or OH* is at least 1 order of magnitude higher than the value on a clean surface. On the Cu(211) surface, unlike Cu(111),[22] the free energy barrier for CO_2 activation via the HCOO* or COOH* pathway by molecular H_2O near the surface is higher than the direct hydrogenation of H atoms on clean and OH- or O-preadsorbed surfaces. In this case, H_2O-derived species, i.e., O* and OH*, are responsible for the enhanced catalytic activity due to their coadsorption, which can attenuate poisoning by HCOO* and reduce the energy barriers. The adsorbed O* on the surface of catalysts can combine with H_2O to form two hydroxyl groups with a low barrier of 0.09 eV.[115] Then, the formation of the Zn···OH/Cu active phase can significantly improve the rate of methanol synthesis by facilitating two key steps, namely, HCOO* and CH_3O^* hydrogenation. The H atom on the hydroxyl group can directly participate in the reaction as a hydrogen source that reacts with CO_2 to form an HCOO* intermediate.[116]

Based on the above understanding, researchers have synthesized a series of catalysts with hydroxyl-rich surfaces that are an order of magnitude more active for CO_2 hydrogenation than their corresponding hydroxyl-free structures.[117−119] However, it is important to note that the higher the coverage of surface hydroxyl groups, the more favorable the RWGS reaction, which may lead to methane production.[120] The hydroxyl groups on the oxide supports can significantly weaken the metal−support interaction and destabilize the catalyst.[120] Therefore, the coverage of surface hydroxyl groups needs to be controlled in order to balance the distribution of the desired products and the stability of the catalysts.

Similar phenomena have also been observed for the hydrogenation of CO_2 to higher alcohols ($C_{2+}OH$), such as ethanol synthesis ($2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$). The promotion of $C_{2+}OH$ synthesis from CO_2 hydrogenation by small amounts of H_2O (<1%) has been observed, and D_2O labeling experiments have shown that water is involved in alcohol formation as a hydrogen source.[121] It has been proposed that H_2O can protonate methanol, which readily dissociates into a CH_x^* species that reacts with CO to form CH_3CO^*, leading to ethanol formation.[121,122]

It should be highlighted that negative effects are also observed when excess H_2O is present during CO_2 hydrogenation, although there is no precise threshold for the concentration of H_2O to cause these effects. It has been observed that methanol formation is significantly suppressed by the presence of H_2O in the feed as the fraction of H_2O increases from 10% to 30%, which is presumably due to the competitive adsorption on the active sites.[123,124] It is also found that the byproduct H_2O during methanol synthesis accelerates the crystallization of Cu and ZnO in the catalysts, leading to catalyst deactivation.[125] For In-based catalysts, an excessive amount of byproduct H_2O can annihilate the oxygen vacancies and sinter In_2O_3.[126,127] In addition, in terms of the influence of product concentration on the reaction rate, methanol has a weaker inhibition effect than water.[103] For CO_2 hydrogenation to higher alcohols, further increasing the H_2O fraction from 1% to 10% leads to a decrease in both CO_2 conversion and C_{2+} selectivity.[121] Under this circumstance, hydrophilic and hydrophobic modification of the CO_2 hydrogenation catalyst may suppress the poisoning effect of H_2O on active sites during product formation.[128,129]

4. H_2O AS A PROMOTOR OR COREACTANT IN CH_4 ACTIVATION

4.1. Selective Oxidation of CH_4 to Methanol. The selective oxidation of CH_4 to methanol has attracted extensive interest from researchers, as the reaction is thermodynamically favorable and can be achieved under mild conditions ($CH_4 + 0.5O_2 \rightarrow CH_3OH$). The reaction mechanism has been

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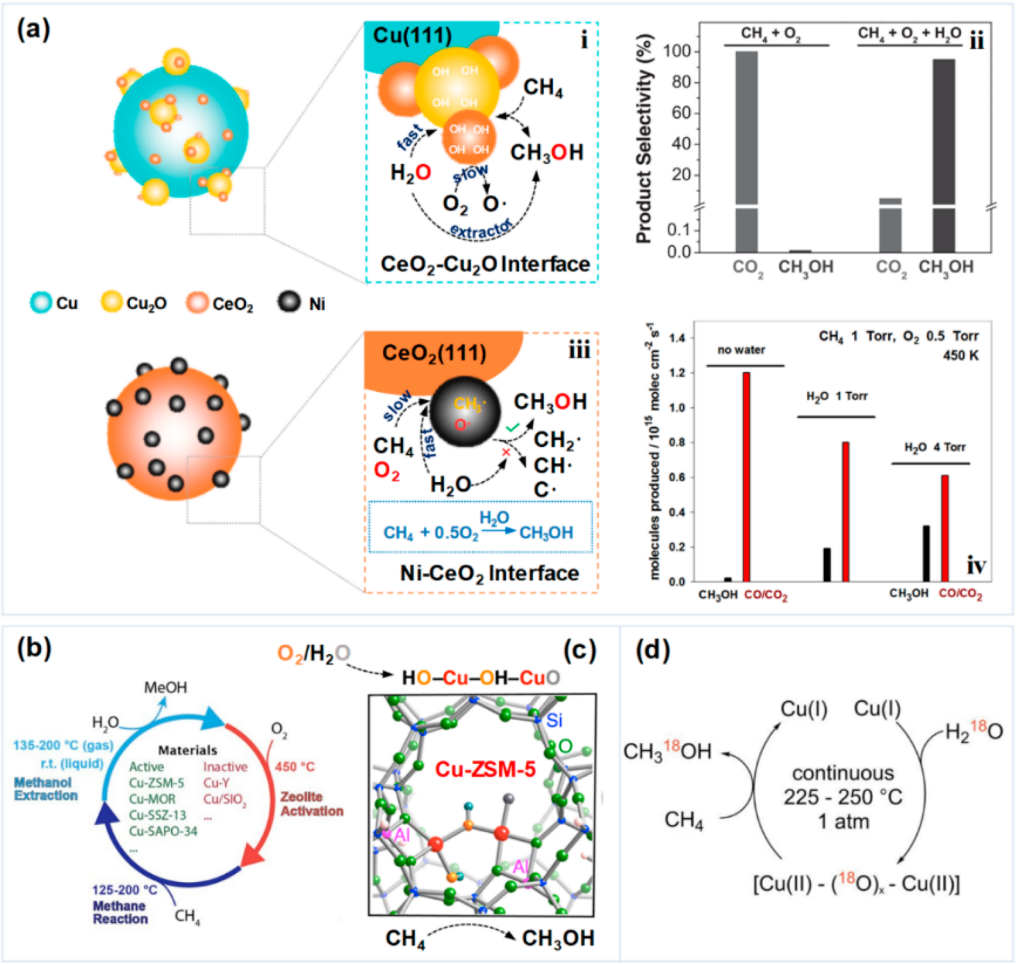

Figure 5. (a) The role of H_2O in interfacial pathways of methane oxidation to methanol over different catalysts: (i) H_2O-promoted interfacial pathways on a CeO_2−Cu_2O catalyst; (ii) selectivity of CH_4 oxidation at 450 K over $CeO_2/Cu_2O/Cu(111)$ on exposure to CH_4 and O_2 with a pressure ratio of 2:1 or CH_4, O_2, and H_2O, with a pressure ratio of 2:1:8; (iii) H_2O-promoted interfacial pathways on a $Ni/CeO_2(111)$ catalyst; (iv) production of methanol on a $Ni/CeO_2(111)$ catalyst as a function of H_2O pressure. The Ni coverage on CeO_2 was ∼0.15 ML. The sample was exposed to 1 Torr of CH_4, 0.5 Torr of O_2, and 0, 1, or 4 Torr of H_2O at 450 K. Panel (a)-ii is adapted with permission from ref 140. Copyright 2020 AAAS. Panel (a)-iv is adapted with permission from ref 133. Copyright 2018 American Chemical Society. (b) The discontinuous catalytic conversion of methane to methanol using copper-based molecular sieves. Effect of H_2O on the selective oxidation of methane to methanol (c) over O_2-bound Cu-ZSM-5, (d) in a flow reactor over Cu-SSZ-13. Panel (c) is adapted with permission from ref 136. Copyright 2016 American Chemical Society. Panel (d) is adapted with permission from ref 139. Copyright 2020 American Chemical Society.

extensively studied, with a focus on the active site, the nature of reaction intermediates, the reaction pathway, and the role of O_2 in the conversion of CH_4 to CH_3OH.[130−133] In general, the presence of H_2O in this reaction can suppress the deep oxidation of methane to CO_2, improve methane activation, and enhance the desorption of methanol.[133−141]

For example, Rodriguez and co-workers[137] report that methane can be activated at room temperature over a $CeO_2/Cu_2O/Cu(111)$ catalyst, forming C, CH_x, and CO_x species on the oxide surface, and the OH groups from H_2O dissociation can saturate the catalyst surface, removing sites that could decompose CH_x fragments and generating centers on which methane can directly interact to produce methanol. Further studies[140] reveal key steps for the promotion of this reaction by H_2O on $CeO_2/Cu_2O/Cu(111)$, finding that H_2O can preferentially dissociate at interfacial Ce sites to form OH, as well as inhibit dissociation of O_2. The active OH* species can generate CH_3OH and H* by reaction with CH_4*. In addition, the adsorption of H_2O is stronger than CH_3OH, which promotes the desorption of CH_3OH and increases selectivity to ∼95% (Figure 5a-ii). Briefly, on $CeO_2/Cu_2O/Cu$ (111), H_2O is a key component in the highly selective oxidation of methane to methanol by playing three fundamental roles in interfacial pathways: (i) blocking the possible conversion of methane and methanol to CO or CO_2 at active sites; (ii) providing an oxygen source to participate in the direct conversion of CH_4 → CH_3OH; and (iii) facilitating the desorption of methanol from the catalyst surface (Figure 5a-i). On $ZnO/Cu_2O/Cu(111)$,[141] the addition of H_2O leads to the defective sites on the oxygen-rich ZnO overlay being stably occupied by OH*, thus hindering the direct oxidation of CH_4 to CO_2 and promoting the extraction of CH_3O* as CH_3OH. Compared to anhydrous conditions, the presence of H_2O leads to higher methane conversion and enhances the overall methanol selectivity.

Similar to the Cu-based catalysts, on Ni/CeO_2 in the absence of H_2O, the products are mainly CO/CO_2 and H_2, while only small amounts of methanol are detected.[133] Methanol selectivity is significantly increased upon addition of H_2O. In the presence of H_2O, $Ni/CeO_2(111)$ exhibits a

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different mechanism of direct conversion of methane to methanol than $CeO_2/Cu_2O/Cu$ (111) (Figure 5a-iii). The chemisorbed OH and H species from the dissociation of H_2O preferentially occupy the Ni active sites. Thus, CH_3* prefers to react with existing O* species to form CH_3O*, which is unlikely to decompose on the Ni sites. The optimal coverage of 15% Ni exhibits only about 35% methanol selectivity, which does not change significantly with an increase in H_2O (Figure 5a-iv). Therefore, the role of H_2O on $CeO_2/Cu_2O/Cu$ (111) as the main oxygen source that also inhibits the adsorption and dissociation of O_2 is more significant than its role on Ni/CeO_2(111), which involves hindering the dehydrogenation of CH_4 derivatives (CH_3* or CH_3O*).

Inspired by natural methane monooxygenases, molecular sieves loaded with first-row transition metals such as Fe and Cu are considered to be some of the best catalyst candidates for this reaction.[142,143] H_2O also plays an important role in the formation of methanol from methane over Fe- and Cu-exchanged zeolites. Cu-based molecular sieves prepared using ion-exchange methods are the most promising catalysts.[138,144] The concept for the conversion of methane to methanol using such catalysts is shown in Figure 5b. By using active oxygen in zeolites as the oxidant, the oxidation can take place even at room temperature, with few byproducts formed. However, the methanol production rate is influenced by the time required for methanol desorption from H_2O, with a full catalytic cycle typically taking more than 10 h.

At low temperatures (483−498 K), the direct and continuous catalytic oxidation of methane to methanol can be reached using oxygen and H_2O as oxidants on a Cu-exchanged molecular sieve, and H_2O is crucial for methanol formation.[145] Over the O_2-bound Cu-ZSM-5 catalyst,[136] H atoms are transferred from the attached H_2O to the bound oxygen molecule to form hydrogen peroxide bridged by a double copper site (Figure 5c). The O−O bond of the peroxyhydrogen species is then cleaved to form oxygen-containing radical intermediates such as HO−Cu−O−Cu−OH and HO−Cu−OH−CuO, which both exhibit more efficient methane activation relative to that of Cu−O−Cu under anhydrous conditions. This mechanism suggests that the coordination effect of H_2O produces active hydroxyl groups that can selectively oxidize methane directly to methanol, but the source of oxygen in methanol is considered to be dioxygen. Similarly, the results of theoretical studies of the selective oxidation of methane to methanol catalyzed by H_2O on Fe/ZSM-5 have shown that H_2O leads to increased activity on the double-coupled $[Fe(\mu\text{-}O)(\mu\text{-}OH)Fe]^+$ and $[HOFe(\mu\text{-}O)\text{-}FeOH]^{2+}$ sites compared to the anhydrous sites.[135] Overall, the role of H_2O in the selective oxidation of methane to methanol over Cu- and Fe-based molecular sieve catalysts is mainly to promote the activation of methane and its further selective oxidation to methanol. On the other hand, the oxygen source for methane oxidation to methanol is also proposed to be mainly H_2O rather than O_2. Isotope-labeled infrared spectroscopy experiments provide evidence that the oxygen in produced methanol is mainly from the H_2O, as shown in Figure 5d.[139] Likewise, Sun et al.[134] also observed that the presence of H_2O not only induces the reaction but also is the main source of oxygen in the produced methanol, proving that H_2O plays an important role by forming active species for methane activation or participating in the selective oxidation of methane.

4.2. Steam Reforming of CH_4. Methane is also an important feedstock to produce H_2. Currently, over 95% of H_2 production is accomplished through methane reforming. The steam reforming of methane (SRM, $CH_4+H_2O \rightarrow 3H_2+CO$) is a predominant industrial process for the production of H_2 and CO, which has been gaining interest.[146] Though this technology was proposed almost 100 years ago, research and industrial efforts to improve catalyst and process design have continued to optimize the reaction system.[147]

The reaction between H_2O and CH_4 occurs in a high-temperature environment (typically 973−1173 K) and is typically catalyzed by metal-based catalysts.[148] The main pathway of SRM involves the adsorption and dissociation of CH_4 and H_2O molecules on active metal sites or supports, as well as the subsequent oxidation of carbon-containing intermediates.[149,150] It is generally accepted that the RDS in SRM is the dissociative adsorption of CH_4, i.e., cleavage of the C−H bond of CH_4 that usually occurs on a metal site,[150−152] while H_2O seems play a supporting role.[153−157] For instance, adsorbed OH from H_2O dissociation may assist in the breaking of the first C−H bond in CH_4,[158,157] and the reactive hydroxyl groups are responsible for the further oxidation of carbon-containing intermediates.[159] However, Vogt et al.[160] find that the activation of CH_4 may not be the only RDS based on isotopically labeled experiments showing the formation of CH_3D upon pulsing D_2O. Their investigation further indicates that, for Ni/SiO_2 catalysts with relatively large Ni nanoparticles (>4.5 nm), the activation of the H_2O becomes kinetically limiting for SRM.[153,161]

Coking and sintering are two major issues leading to catalyst deactivation in SRM,[147] which are both related to the presence of H_2O. It is generally accepted that H_2O is directly involved in reducing carbon deposition during the SRM reaction.[162,163] In this case, the adsorption of H_2O and oxidation of carbon species by H_2O-derived species play a vital role in carbon suppression.[163,164] A DFT study shows that a MnO−Co catalyst with a strong adsorption capability for H_2O is crucial for inhibiting carbon deposition.[163] In another example, adding CeO_2 into Rh/Al_2O_3 accelerates the reaction between H_2O and carbon species, leading to an enhancement in the overall SRM reaction rates.[164] In addition, the stable conversion rate and product selectivity also depend on the feed ratio of H_2O/CH_4.[165,166] For a low-temperature SRM on a Ni/TiO_2 catalyst, s relatively high steam feed (H_2O:CH_4 = 3) can effectively drive carbon gasification and stabilize the SRM performance.[165] It should be highlighted that although higher steam feed can effectively reduce the extent of carbon deposition, this strategy may also deactivate catalysts by destroying the internal structure of the support material or leading to the agglomeration of metallic catalyst particles.[165,167] It has been observed that the presence of a hydroxylated Ni surface due to the reaction between H_2O and Ni leads to severe sintering of Ni via Ostwald ripening.[167]

Overall, there should be a balance between the activation of CH_4 and H_2O. The imbalanced dissociation of CH_4 and H_2O can induce carbon deposition and metal sintering, and thus lead to the deactivation of Ni catalysts.[168−171] To improve the performance of Ni-based catalysts, many efforts have been made, including the modification of electronic properties of Ni by doping another metal to form a bimetallic structure and the stabilization of Ni nanoparticles by introducing reducible oxide supports,[168,170,172−175] which not only provide active sites for the dissociative adsorption of H_2O but also gasify carbon

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deposits. Similar strategies have also been applied to other catalysts to improve their performance for SRM. For example, by performing *in situ* X-ray absorption spectroscopy measurement, Duarte et al.[173] reported that the oxidation state of cerium is partially reduced (Ce^{4+} to Ce^{3+}), and Rh is completely reduced for the $Rh/CeO_2-Al_2O_3$ catalyst under SRM conditions. The reduced Ce^{3+} reacts with H_2O and reoxidizes to Ce^{4+}, which can readily react with CH_4 to form Ce^{3+}. In this way, H_2O works cooperatively with CeO_2 in the $Rh/CeO_2-Al_2O_3$ catalyst to promote the reaction by altering the oxidation state of CeO_2, which helps stabilize the Al_2O_3 structure by forming $CeAlO_3$ and maintaining the dispersion of the active phase.

It should be highlighted that almost all the above-mentioned mechanisms for SRM are proposed on the basis of experiments performed at relatively low temperatures (≤873 K), which are much lower than the industrial operating temperatures (>1073 K). Since the activations of both H_2O and CH_4 strongly depend on the reaction temperature, the understanding of reaction mechanisms of SRM under realistic conditions, especially regarding the role of H_2O, requires further studies. However, experimental investigation of reaction mechanisms at temperatures of >1073 K is extremely challenging.

4.3. Oxidative Coupling of CH_4. In the oxidative coupling of methane (OCM) reaction, methane can be coupled to produce C_2 hydrocarbons (C_2H_6 and C_2H_4) using O_2 as the oxidant.[176] In contrast to nonoxidative coupling of methane (NOCM), OCM is free from thermodynamic constraints.[177] However, a high operating temperature is still required to activate CH_4 and obtain appreciable C_2 hydrocarbon productivity, which inevitably leads to the further oxidation of the desired products to CO_2.

The addition of H_2O is found to result in higher reaction rates and C_2H_6/C_2H_4 yields over the extensively studied MnO_x-Na_2WO_4/SiO_2 catalysts.[178−180] It is proposed that the C−H bond activation can be mediated by either surface atomic oxygen species or surface OH* radicals originating from H_2O, which yield CH_3* radicals, followed by recombination of the latter to C_2H_6. The higher reactivity is suggested to be related to the presence of the more reactive surface OH* radicals. In addition to accelerating methane conversion, H_2O can also play a positive role in suppressing the formation of certain surface oxygen species that react with CH_3* radicals to produce CO_x.[181] The presence of H_2O promotes the dissociation of O_2 on the surface of the catalyst, which suppresses the direct methane oxidation to CO_2 (Figure 6).[182,183]

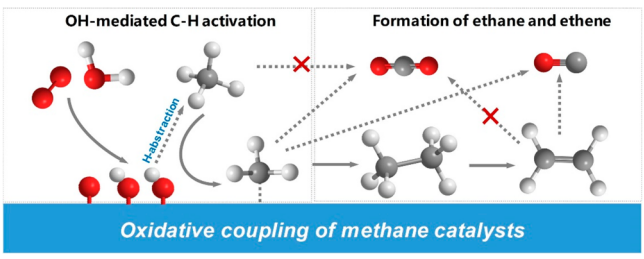

Figure 6. H_2O-mediated pathways for the OCM reaction. Reproduced with permission from ref 182. Copyright 2020 American Chemical Society.

5. OUTLOOK AND PERSPECTIVES

In nonaqueous reactions, the presence of H_2O is often unavoidable, as is the case when H_2O molecules are present in the reactants (either as an impurity or a coreactant), adsorbed on the surface of catalysts, or formed as a reaction byproduct, etc. As summarized in this Perspective (Figure 7), H_2O can play important chemical and catalytic roles in the catalytic conversion of C_1 molecules (CO, CO_2 and CH_4). Some of the positive effects of H_2O include the following: (i) adsorbing onto the catalyst surface and interacting with reactants to alter the pathway and increase the reaction rate; (ii) decomposing into H*, OH*, and O* species to serve as key intermediates in the conversion process; (iii) forming hydrogen bonds or other noncovalent interactions with reactants to enhance the reactivity and selectivity; (iv) acting as a hydrogen or oxygen source to participate in the reaction.

For catalytic reactions involving CO, H_2O can be both a reactant and a promoter for H_2 production in the WGS reaction by forming the COOH intermediate, which lowers the reaction energy of the rate-determining step. Similarly, a promotional role of H_2O has also been proposed for CO oxidation over reducible oxide supported catalysts by facilitating the activation of O_2 and the formation of COOH*. H_2O can also participate in the reaction and influence the reaction kinetics in FTS by acting as a proton transfer agent. Over the past few decades, advances in developing *in situ*/*operando* characterization and computational simulations have improved the molecular-level understanding of the structure and dynamics of H_2O on solid surfaces. Despite these significant efforts, it remains challenging to experimentally determine the configuration of H_2O on the catalyst surface under the reaction conditions. Recently, Yuan et al.[184] have reported the structural reconstruction of the anatase TiO_2 surface in the presence of H_2O and CO using *in situ* environmental TEM. The high spatial and temporal resolution of TEM enables monitoring of the adsorption and dissociation of H_2O on the TiO_2 surface, which leads to the formation of twinned protrusions that react with CO to form H_2 and CO_2 (WGS). Likewise, ultrafast infrared spectroscopy[185] that probes the stretching mode of the OH group provides opportunities to study the hydrogen bonding dynamics of H_2O during catalytic reactions.

For the hydrogenation of CO_2, H_2O plays a crucial role in methanol synthesis as an important byproduct. H_2O can play the following three promoting roles in CO_2 hydrogenation reactions: enhancing the formation and further conversion of intermediates via H-transfer, modifying the catalyst surface to form an OH-containing active phase, and promoting the conversion of CH_3O* via the hydrolysis reaction. All three roles are related to the presence of H_2O-derived species (O*, OH*, and OOH*), though details on the reaction pathway are still unclear. Precise identification of the H_2O-mediated microenvironment on catalysts is still a major challenge in both theoretical and experimental studies. It should be highlighted that the enhancing effects of H_2O on methanol formation are observed only for systems with trace amounts of H_2O. Therefore, regulating the conversion of surface intermediates mediated by H_2O while keeping the active sites and structure of the catalyst unchanged is a major challenge for CO_2 hydrogenation. It is worth emphasizing that H_2O produced via hydrogenation on the catalyst surface shows a stronger inhibition effect than produced methanol. In this

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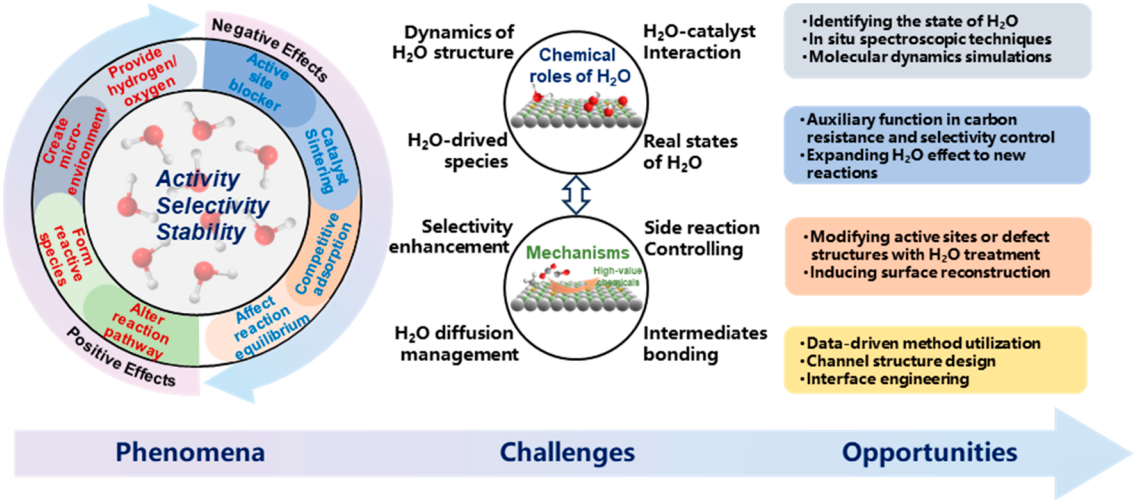

Figure 7. Challenges and opportunities of understanding H_2O in catalytic conversion of C_1 molecules.

case, both the microscopic point of view to regulate the microenvironment on the surface of the catalyst and the macroscopic point of view to control the chemical equilibrium via enhancing water diffusion are important for designing a high-performance catalyst.

For the catalytic conversion of CH_4 to syngas, methanol, or other hydrocarbons, H_2O as either a coreactant or a promoter can effectively regulate the selective conversion of CH_4. H_2O can promote these reactions from several aspects: creating a weak oxidant atmosphere to avoid the deep oxidation of methane, dissociating at the active sites to form a hydroxyl-rich surface for selective conversion of CH_4, attenuating the ability of the active site to fully dissociate all of the C−H bonds in CH_4 to avoid carbon deposition on the catalysts, and promoting the desorption of products. Specifically, H_2O as a weak oxidant can neutralize the strong oxidation effect of oxygen and inhibits the oxidation of methane to CO_2 by producing H_2O-derived surface reactive oxygen species. For SRM, the presence of H_2O increases the reaction rate by facilitating the dissociation of CH_4 and promoting surface reactions. It also helps maintain catalyst stability by reducing the formation of carbon deposition on the catalyst surface, while the H_2O/CH_4 feed ratio is also critical for stabilizing catalytic conversion and product selectivity. Because H_2O typically adsorbs more strongly than methanol, H_2O also facilitates the desorption of methanol from the catalyst surface in CH_4 oxidation to methanol. However, a further understanding of the role of H_2O-derived species in reactions involving the selective conversion of CH_4 is needed to regulate product selectivity during CH_4 conversion by using H_2O as either a promoter or a reactant.

Although a H_2O-mediated microenvironment often leads to positive effects in catalytic reactions, direct experimental evidence and detailed explanations of these effects still require further research efforts. In some reactions, H_2O may also slow the rate, depending on the form and concentration of H_2O, competitive adsorption mechanisms, and other induced species. In addition to activity and selectivity, the stability of catalysts in the presence of H_2O, a key parameter of catalytic performance, has not been systematically studied. To better understand and fully exploit the positive effects of H_2O in gas-phase reactions, more studies should be performed in the following areas:

(1) *Understanding reaction pathways for H_2O-mediated conversion of C_1 molecules under realistic conditions.* The combined utilization of *in situ/operando* experimental techniques and theoretical simulations will be critical in understanding the reaction mechanisms and the key steps controlling activity and selectivity. Molecular/atomic-level understanding based on active sites and surface species detected under reaction conditions is essential to design a state-of-art catalyst. At present, the proposed pathways for the involvement of H_2O in the conversion of C_1 molecules mainly depend on DFT calculations.[6,21,89,186] Most of the H_2O structures have been observed on clean and well-defined single crystal surfaces under UHV conditions.[187,188] Systematic studies of the structure of H_2O under ambient/realistic conditions face many difficulties due to the dynamic nature of the interfaces, but represent the next frontier for fundamental research.[189] Future experimental measurements should focus on the identification of active reaction intermediates by *in situ* spectroscopic techniques.[7,116] Meanwhile, more realistic models based on experimental reaction conditions should also be applied to theoretical simulations, for which the combination of kinetic Monte Carlo or molecular dynamics simulations with DFT calculations is necessary.[140] It is noteworthy that the theoretical modeling of H_2O molecules participating in heterogeneous catalytic reactions in different states should minimize the gap between theory and experiments. Although H_2O molecules are relatively simple, the presence of molecular forces between them makes it challenging to model them correctly. Therefore, sorting out the various forms of H_2O (H_2O molecules, H_2O clusters, OH/OH, H/H, etc.) and their influence on the energetics of elementary reaction steps is crucial for understanding the reaction mechanisms.

(2) *Developing characterization techniques to study catalyst surface-H_2O molecule-intermediate species.* The lack of suitable characterization techniques to identify the structure of solid-H_2O interfaces, especially *in situ* methods with high spatial and temporal resolution, limits the understanding of catalytic systems in the presence of H_2O. Traditional surface-sensitive probes,

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such as soft X-rays and low-energy electrons, are not capable of penetrating the aqueous layers due to their small mean free path. Therefore, developing experimental methods to identify the interfacial behaviors and elucidate the dynamic processes of H_2O or H_2O-derivatives near the solid surface are necessary to enhance understanding. Methods to perform experiments using scanning probe microscope and surface science studies on well-defined model surfaces are of great significance.

(3) *Investigating stability and selectivity of catalysts under reaction conditions.* Catalyst stability in the presence of H_2O is one of the critical metrics of catalytic performance in addition to activity and selectivity. For example, experimental and computational studies regarding carbon removal by H_2O have been performed for decades in the field of methane reforming.[190,191] In addition to inhibiting coking, the presence of H_2O can also increase the available protons to promote the production of CO and H_2. Polycyclic aromatics have been shown to be the precursors for coke formation, which causes the deactivation of most zeolite catalysts in C_1 molecule conversion. In the highly selective conversion of CO_2 to aromatics over tandem catalysts, the presence of H_2O significantly alleviates deactivation of the catalyst by suppressing the formation of these polycyclic aromatics.[192] Moreover, methane dehydroaromatization (MDA) catalysis has potential to replace existing processes due to the increasing global production of natural gas (and biogas). However, the major obstacle for this process is the rapid deactivation of catalysts due to high coke selectivity. The addition of H_2O has been considered to inhibit coking and improve the lifetime of MDA catalysis in several studies.[193,194] H_2O plays a vital role in maintaining the activity of heterogeneous catalysts by oxidizing carbon to gas-phase CO or CO_2. However, as H_2O concentration increases, the total selectivity of valuable hydrocarbons (aliphatics and aromatics) decreases significantly and CO becomes the dominant product. Therefore, it is important to understand the effect of H_2O concentration on controlling the catalytic selectivity in these H_2O-mediated reactions.

(4) *Enhancing catalytic activity with H_2O-mediated surface reconstruction of catalysts.* The cocatalysis effect of H_2O on the catalyst surface is related not only to the reaction system but also to the properties of the catalyst. In some cases, the activity of supported metal nanoparticles depends on their surface structure and exposed sites, and can be promoted by modifying specific types of sites or defect structures.[3,11] For example, steam treatment leading to the formation of twin crystals in Pd-based catalysts for methane catalytic oxidation can increase the grain boundary density and catalytic activity.[195] Such grain boundaries have very high stability, and the reaction rate at the grain boundary sites is 2 orders of magnitude higher than that at the intrinsic catalytic sites on Pd/Al_2O_3. Theoretical calculations reveal that the stress formed by the twin crystal defects is the primary factor in the enhanced catalytic activation of the C−H bond. Indeed, double boundaries and grain boundaries are some of the most stable defects on metal surfaces and can act as active sites for some reactions.[195,196] Although grain boundaries have been studied as potential defects with catalytic activity, little is known about how they can be generated via interaction with H_2O. On the other hand, as a byproduct in CO_x hydrogenation, H_2O has a strong oxidative and destructive effect on the active phase (Fe^0/FeC_x) in Fe-based catalysts, and can also induce oxidation and sintering of the metallic Co phase in FTS.[9,197] The presence of excess H_2O is detrimental to the stability of carbide catalysts, while moderate amounts can instead enhance their formation and stability.[198] Therefore, it is important to elucidate the positive or negative effects of H_2O-induced structural changes on catalytic stability and performance in order to rationally modify the synthesis route and reaction atmosphere to optimize the effect of H_2O.

(5) *Expanding H_2O-mediated C_1 conversion to other gaseous phase reactions.* The effect of H_2O on heterogeneous catalytic systems should be further expanded beyond the conversion of C_1 molecules. It is necessary to develop a systematic understanding of which reactions undergo strong or weak promoter effects due to H_2O mediation, and to develop a universal basic theory that can be applied to other heterogeneous catalytic reactions. The correlation between H_2O addition and catalytic activity should be investigated by combining experiments and theory focused on structure−activity relationships.

(6) *Applying data-driven methods to understand complex roles of H_2O.* The dynamic nature of H_2O may also result in its multiple roles in one catalytic system. Quantification of each contribution can be challenging, requiring a combination of experimental kinetic assessments and computational studies. In recent years, the advancement of big data and machine learning (ML) has led to their applications in heterogeneous catalysis.[199] Using theoretical simulations and experimental observations to grow the database and provide guidance for ML training, data-driven ML methods offer additional tools to predict and explain the complex nature and roles of H_2O-derived species in the catalytic conversion of C_1 molecules.

(7) *Learning from electrocatalytic studies to further understand the role of H_2O.* Although the current Perspective focuses on the effects of H_2O in thermocatalytic reactions, it is important to point out that H_2O also plays significant roles in electrocatalytic conversion of C_1 molecules, including CO_2, CO, and methanol. H_2O is probably the most ubiquitous molecule in electrochemical systems because almost all electrocatalytic reactions occur in aqueous environments, and H_2O and its dissociated products (OH^- and H^+) participate either directly or indirectly in electrochemical reactions involving C_1 molecules. The presence of the water layer at or near the electrocatalysts also modifies the local electrochemical potential that in turn regulates the electrochemical activity and selectivity. Information gained from electrochemical studies should help further elucidate the roles of H_2O in thermocatalysis.

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Notes

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