

Heterogeneous Catalysis in Water

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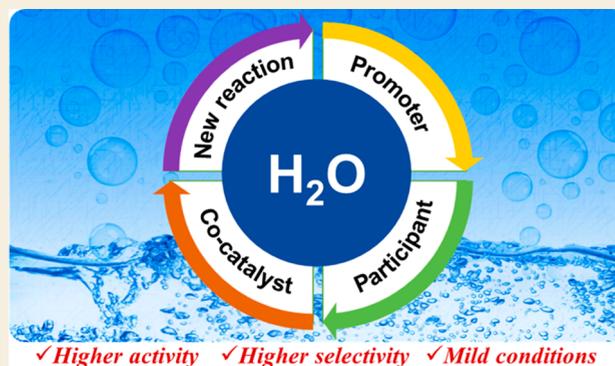
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ABSTRACT: Heterogeneous catalytic processes produce the majority of the fuels and chemicals in the chemical industry and have kept improving the welfare of human beings for centuries. Although most of the heterogeneous catalytic reactions occur at the gas–solid interface, numerous cases have demonstrated that the condensed water near the active site and/or the aqueous phase merging the catalysts play positive roles in enhancing the performance of heterogeneous catalysts and creating novel catalytic conversion routes. We enumerate the traditional heterogeneous catalytic reactions that enable significant rate/selectivity promotion in the aqueous phase or adsorbed micro water environment and discuss the role of water in specific systems. Some of the novel heterogeneous reactions achieved with only the assistance of the aqueous phase have been summarized. The development of reactions with the participation of the aqueous phase/water and the investigation of the role of water in the heterogeneous catalytic reactions will open new horizons for catalysts with better activity, improved selectivity, and novel processes.

KEYWORDS: heterogeneous catalysis, water, promotion effect, aqueous-phase reaction, hydrogen production, CH₄ oxidation, Fischer–Tropsch synthesis



1. INTRODUCTION

“Water that bears the boat is the same that swallows it up (Xunzi)”

This old Chinese motto was recorded in the literature with a long history of 2500 years. In this motto, water is a metaphor for the people and the boat refers to the ruler. It advocated a dominating wisdom to utilize the constructive factors of the people and also be aware of their destructive power. Similarly, in the area of catalysis, the real water has been frequently reported to be a destructive factor which shortens the lifetime of catalysts, reduces the production of desired compounds, reacts with the intermediates and products, causing side reactions, and influences the characterization of working catalysts.^{1–3} Alternatively, the positive properties of water, which benefit the catalytic performance by significantly promoting the reaction rate and selectivity, have been reported widely but are still underestimated.^{4–6} Therefore, in order to fully exploit the advantages of water in a catalytic reaction and prevent potential drawbacks, the design of the reaction system and scientific insights into the reaction mechanism are essential prerequisites.

The positive role of water in a catalytic reaction can be classified into noncatalytic and catalytic effects. From a noncatalytic aspect, water is a green, nontoxic, and inexpensive solvent that obeys the principles of green chemistry.⁷ Meanwhile, as an immiscible solvent with respect to the traditional nonpolar organic solvents, water sometimes facilitates the

product separation as well as catalyst recycling. For example, in the olefin hydroformylation reaction, Rh-TPPTS complexes can be extracted to the aqueous phase after a reaction by a simple acidification post-treatment to achieve high recycling efficiency.⁸ In addition to these noncatalytic effects, numerous cases have demonstrated that water can work as a reactant and even a cocatalyst in heterogeneous catalytic reactions, promoting reaction rates and product selectivity. Especially, aqueous-phase reactions have become game changers in a variety of small-molecule (such as methane) upgrading reactions, enabling the production of value-added chemicals from inexpensive feedstocks that is difficult or even impossible to achieve in gas-phase reactions.

The special role of water in the catalytic reactions has been recognized for a long time. Even during the early times of modern chemistry, Fulhame recorded an accelerated reaction rate between gold and sulfurated hydrogen in humid air.⁹ Gedye has reviewed the promoting effect of water in chemical reactions, which focused on both experiments and theory.⁹ The positive

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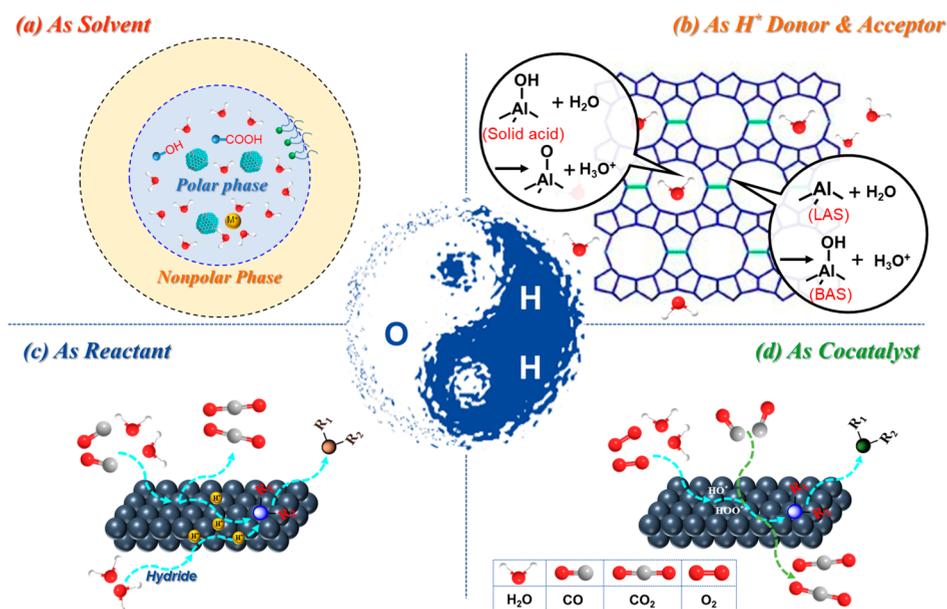


Figure 1. Schematic presentation of selected functions of water in a heterogeneous catalytic system: (a) working as a solvent to influence the solubility, transport behaviors, and solvation effects of reactants, intermediates, and products; (b) working as a proton donor/acceptor and as an influential factor for heterogeneous acid/base catalysts; (c) working as a reactant for the *in situ* production of active H^* in hydrogenation reactions; (d) working as a cocatalyst to produce highly active oxidizing species in diverse oxidation reactions.

effects of water in organometallic¹⁰ and environmental reactions^{11,12} have also been reviewed in a series of classic reviews. Recently, Resasco and co-workers presented a comprehensive review on the function of water in catalytic reactions and detailed water-mediated heterogeneously catalyzed reactions.⁴ In this perspective, we will briefly review the structure and function of water in catalytic reactions in section 2 and pay special attention to the important heterogeneous catalytic reactions that occur in the aqueous phase, including alcohol or biomass-derived polyol reforming, CH_4 activation, and some other C_1 chemistry reactions in section 3. The special promotion effects of water in these reactions are analyzed in detail. In section 4, we summarize the novel catalytic processes reported recently in which water works as both the reactant and reaction medium. Microscale water environment condensed or adsorbed on the heterogeneous catalysts that enhances the reaction performance is stressed in section 5. The scope discussed will be limited to the classical heterogeneous thermal catalysis, and only a few cases of photocatalyst that are closely relevant to the topic are included. We hope this review will shed light on the better utilization of water/aqueous phase, since water is not expensive, is easy to use in post-treatment in catalytic reactions, and achieves better activity, selectivity, and the development of novel processes.

2. THE STRUCTURE, PROPERTIES, AND CATALYTIC FUNCTIONS OF WATER AS THE REACTION MEDIUM

Water is a polar molecule with two hydrogen atoms linked to one oxygen atom. Under ambient conditions, the length of the O–H bond is approximately 0.96 Å and the angle between two O–H bonds is about 104.5°. Due to the nonlinear structure of a water molecule, the positive and negative charge centers do not overlap, giving the molecule a large electric dipole moment of 1.85 D.

The strong polarity of water makes it easy to solvate inorganic salts and hydrophilic organic compounds, which facilitates the transport of soluble reactants to the active sites (Figure 1a).

When it is used in a nonpolar reaction, water can form strong polar regions or emulsions that influence the diffusion behavior of guest molecules and could increase the local concentration of hydrophilic molecules and strongly polar functional groups. With this property, the reaction preference and selectivity on certain catalysts can be tuned.^{13,14} In addition to the ability to influence the transport behavior and solvation manner of reactants and products, an aqueous medium can also modify the structure and energy of reaction intermediates and transition states.¹⁵ Due to the different degrees of stabilization of the reactants, intermediates, and transition states, the reaction barrier and thermodynamics of a reaction or certain elementary steps can be changed, which accounts for a variety of water-promoted catalytic reactions,^{16,17} such as hydration and dehydration reactions in the aqueous phase.^{18,19}

Water is a good proton donor and acceptor (Figure 1b). As a result, water is both a Brønsted acid and base. In an aqueous solution, the acidic or basic properties of relatively weak acid/base catalysts can be distinguished by different electrolyzed degrees of water. In contrast, the strong acid/base will be leveled to the same degree. Similar to the case for liquid acids, solid acids such as zeolites can also enhance the ionization of water and make the aqueous reaction medium exhibit the catalytic behavior of liquid acids.^{20,21} Meanwhile, the existence of water can also change the type of acid sites. For example, water tends to protonate the Lewis acid site and transform the Lewis acid sites (LAS) into Brønsted acid sites (BAS) in the aqueous phase.^{22,23} Due to these properties, aqueous-phase acid/base reactions generally exhibit special characteristics different from those of gas-phase reactions.

Water can be the reactant in heterogeneous catalytic reactions (Figure 1c). In addition to hydration, hydrolysis, and water-gas shift reactions in which water directly participates in the reaction, water can also act as the hydrogen source in hydrogenation processes operated in the aqueous phase. In this *in situ* hydrogen formation strategy, certain reductants, such as a metal hydride,²⁴ carbon monoxide,^{25,26} and alcohols,²⁷ react

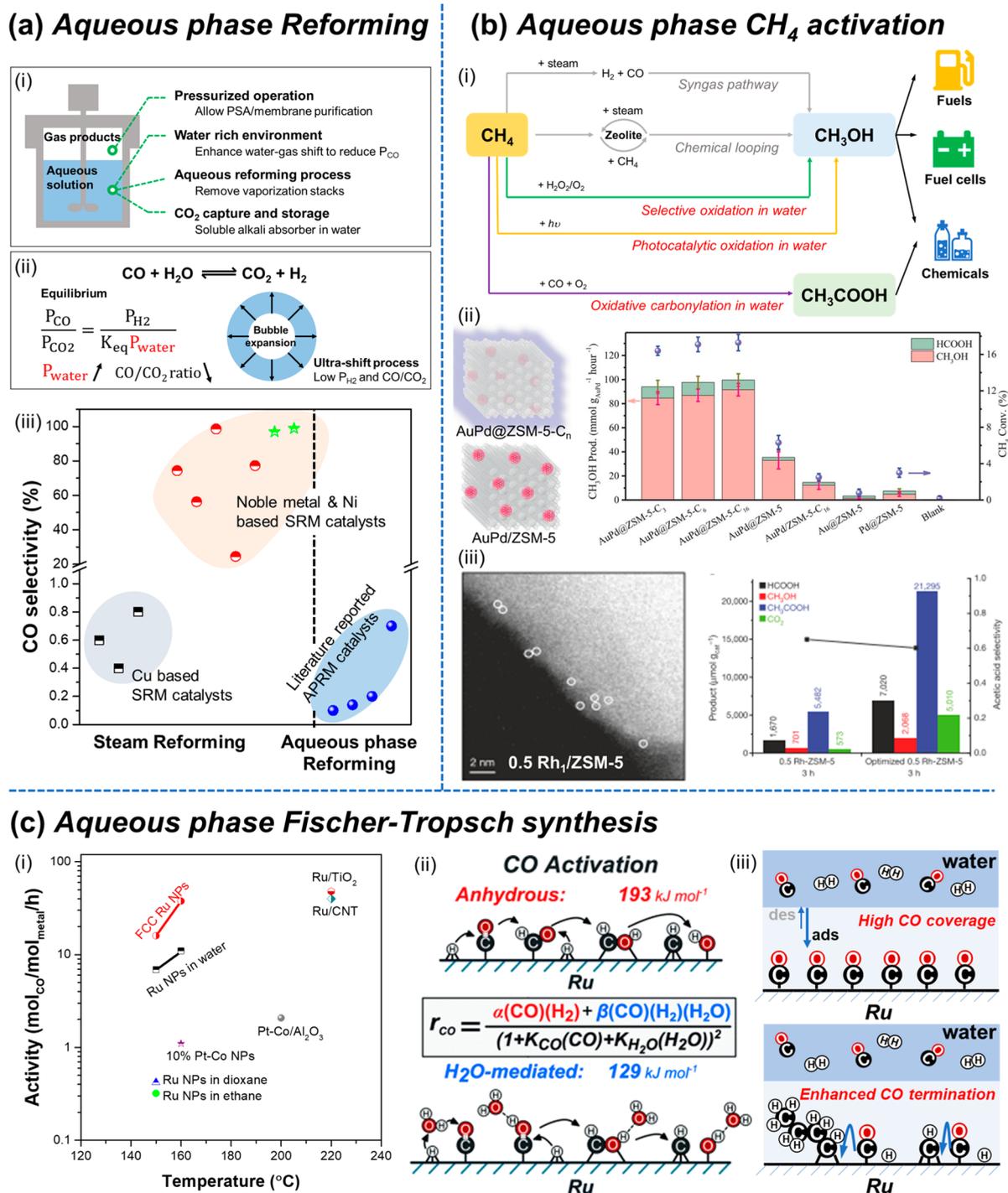


Figure 2. Schematic presentation of water-promoted heterogeneous reactions in the aqueous phase. (a) Aqueous reforming reaction of biomass-derived methanol and polyols: (i) the advantages and privileges of aqueous-phase reforming,⁵⁰ (ii) the “ultra-shift” achieved in the aqueous-phase reforming process that reduces the CO concentration,⁵⁰ (iii) a comparison of the byproduct CO level of reforming catalysts in aqueous-phase and steam reforming reactions.^{37,49,53,55} (b) Methane activation in water: (i) summary of the conversion routes of methane in the aqueous phase via partial oxidation and oxidative carbonylation reactions; (ii) hydrophobic zeolite encapsulated AuPd catalyst for highly efficient methane partial oxidation;⁶⁹ (iii) Rh₁/ZSM-5 catalysts and the methane oxidative carbonylation reaction it catalyzed.⁶⁷ (c) Aqueous-phase Fischer–Tropsch synthesis: (i) comparison of the catalytic activity of different Ru- and Co-based catalysts at varying working temperatures in the aqueous phase and an organic medium;^{83,84,90,93} (ii) water-assisted CO dissociation over Ru-based catalysts;⁹⁵ (iii) function of enhanced CO surface coverage and CO termination probability in the aqueous-phase reaction.

with water to release H₂ or highly reactive atomic hydrogen in water on the surface of catalysts that further participates in the hydrogenation reaction.²⁸ Similarly, such a tandem hydrogenation strategy can be applied to an electro- or photocatalytic

reduction process in which water splitting serves as the hydrogen formation reaction.^{29–31}

Water serves as a cocatalyst in a variety of oxidation reactions (Figure 1d). On reaction with oxygen on the surface of catalysts

or on stimulation by an electron field³² and/or photoradiation,³³ water can be activated to form highly reactive $\bullet\text{OH}$ and $\bullet\text{OOH}$ radicals.³⁴ These species are identified as the key intermediates for variety of oxidation reactions in the aqueous phase: for example, the activation of inert C–H bonds.¹⁷ In low-temperature CO oxidation reactions, the existence of these species has been identified as the main reason for the low-temperature activity of catalysts in the presence of moisture.⁵

The special physical and chemical properties of water give the aqueous phase various properties in heterogeneous catalytic reactions. To utilize these properties, a significant promotion of the catalytic performance has been obtained in the conversion of a series of important and high-economic-impact substrates. In the following section, we will summarize the catalytic systems promoted by water feeding/dosing and discuss the role of water in each reaction.

3. THE PROMOTION OF TRADITIONAL CATALYTIC REACTIONS IN THE AQUEOUS PHASE

3.1. Aqueous-Phase Hydrogen Production from Primary Alcohol and Biomass-Derived Polyol Reforming

Hydrogen is considered to be the major sustainable alternative energy resource in the future.³⁵ The policies targeting reducing carbon emissions in the near future have placed the renewable hydrogen energy as one of the major components of the future energy strategy.³⁶ Hydrogen produced from biomass-derived alcohols and carbohydrates is considered to be renewable hydrogen.^{37–40} The conversion of alcohol hydrogen in a distributed device is a potential solution of hydrogen production for underdeveloped regions, where there is a lack of H₂ distribution networks and transportation/storage infrastructures.⁴¹ The alcohol molecules can serve as a high-density hydrogen storage medium for satellite facilities and mobile application scenarios.⁴² Therefore, the development of efficient catalytic systems for hydrogen production from alcohols, especially under mild conditions, has attracted significant interest in the past two decades.

The reaction of alcohols with water not only releases the hydrogen in the organic substrates but also extracts the hydrogen from water (Figure 2a). Both steam reforming performing at the gas–solid interface and aqueous-phase reforming can be used to convert low-boiling-point alcohols into hydrogen.^{43–45} From an engineering standpoint, aqueous-phase reforming does not need to vaporize water and alcoholic compounds, which reduces the energy consumption and simplifies the system. The pressurized working conditions (generally 15–50 bar) of the aqueous phase also benefits H₂ separation using facile PSA or membrane techniques. An aqueous-phase reaction facilitates the addition of soluble alkaline adsorbates and CO₂ capture (Figure 2a–i).⁴⁶ In comparison with gas-phase reforming, the aqueous-phase reaction has a thermodynamic advantage. The enhanced water-gas shift reaction in the aqueous phase is able to significantly reduce the CO concentration.^{47,48} Additionally, the suppressed partial pressure of CO₂ and H₂ within the bubbles can further push the equilibrium forward to achieve a better CO removal efficiency (Figure 2a–ii). As a result, the concentration of the CO impurity in the H₂ produced from APR processes is generally below 1% (Figure 2a–iii).^{49,50}

Despite the advantages listed, the choice of the catalyst structure is essential for a successful aqueous-phase hydrogen production system. In methanol reforming, the synergy of the

C–H and O–H bond cleavages and the water-gas shift reaction is the central factor that determines the hydrogen evolution rate. Although Cu-based catalysts are widely used in steam reforming systems due to their well-balanced catalytic properties in the aforementioned steps,^{51,52} due to the poor stability of Cu under hydrothermal conditions, scientists have moved to more stable noble-metal-based catalysts to construct the aqueous-phase reforming catalysts. For example, Dumesic and co-workers have proposed that the catalyst Pt/Al₂O₃ is a potential candidate. The hydrogen evolution rate reached 40 mmol_{H₂} g_{cat}^{−1} h^{−1} at only 225 °C.³⁷ Other high-performance oxide-supported catalysts such as Pt/Ga₂O₃ and Pt/SiO₂ have been introduced to the reforming system due to their excellent hydrogen production activity.⁵³ In comparison with steam-reforming catalysts using a noble metal and Ni as active sites,^{53,54} aqueous-phase reforming has successfully reduced the CO impurity concentration in the exhaust from 20–100% to less than 1% (Figure 2a–iii), which may introduce revolutionary changes in on-site hydrogen production processes. Recently, Ma et al. have reported that a face-centered-cubic structure molybdenum carbide supported Pt is a highly active APR catalyst of methanol.⁴⁹ In comparison with the Pt/Al₂O₃ catalyst, the atomically dispersed Pt on α -MoC exhibited an H₂ production turnover frequency at 18460/h only 190 °C, nearly 2 orders higher than that of the Pt/Al₂O₃ catalyst under the same conditions.⁴⁹ The temperature-programmed surface reaction (TPSR) and DFT calculations revealed that the excellent performance of the Pt₁/ α -MoC originates from an efficient low-temperature water dissociation to form surface hydroxyl species on the carbide support, high C–H cleavage activity on the Pt atom, and the reforming of CO with hydroxyl groups at the Pt– α -MoC interface. The experiment also suggested that water enhanced the dissociation of C–H bonds, which further prevents the poisoning of active molybdenum carbide surfaces by stable oxygenates. Additionally, the Ni atoms can also work as the C–H cleavage centers. Benefiting from the α -MoC substrate, the activity of Ni/ α -MoC reached 171 $\mu\text{mol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$, 6 times higher than that of Pt/Al₂O₃ at 240 °C.⁵⁵ The CO selectivity was also successfully suppressed to the 100 ppm level.

For polyols that are hard to evaporate, aqueous-phase reforming is a more suitable strategy to produce hydrogen and prevent potential side reactions such as decomposition and coking at high temperatures. In the polyol steam-reforming reaction, the reaction temperature may be over 823 K.⁵⁶ It has been observed that an increase in the partial pressure of steam in the feed can significantly inhibit the formation of CO,⁵⁷ which indicates that the use of water as the medium may benefit the hydrogen evolution. When the reaction occurred in the aqueous phase, benefiting from the water-gas shift reaction and the assistance of OH in the cleavage of C–C and C–H bonds, Dumesic and coauthors successfully reduced the reaction temperature of polyol reforming and prevented the formation of byproducts.³⁷ With an increase in the carbon numbers in the alcohol molecules, the ability of C–C bond cleavage becomes the necessary property of the reforming catalyst to prevent the formation of undesirable hydrocarbon byproducts.⁴⁰ On the basis of this consideration, an evaluation of the metal centers has been performed and the effectiveness of the metal center has been found to be in the sequence Pt \approx Ni > Ru > Rh \approx Pd > Ir.⁵⁸ Unlike the steam-reforming reaction, reducible oxide (TiO₂, CeO₂, etc.) supported Pt catalysts exhibit relatively low activity in the aqueous-phase reforming of ethylene glycol and other biomass-derived polyols (such as glycerol and sorbitol), which is

probably due to the deactivation of these reducible materials under hydrothermal conditions. Silica, alumina, zeolite oxides, and tin-promoted alumina were proven to be relatively good supports.⁵⁹ The well-balanced Pt/Al₂O₃, Ni–Sn, and Ru–Sn are effective catalysts for polyols, as reported in the literature.⁶⁰

3.2. Promotion Effect of Water in Aqueous-Phase CH₄ Activation

Methane (CH₄), the principal component of natural gas and shale gas, is not only an energy supply but also an abundant C₁ feedstock for the chemical industry. Currently, the conversion of methane into liquid fuels, olefins, and oxygenate chemicals (such as methanol) is mainly realized through a mature pathway of methane to synthesis gas and then to downstream products (Figure 2b-i).^{61,62} However, the production of syngas from methane is energy-intensive, consuming over 40% of the total energy cost and generating a large amount of CO₂ emissions.⁶³ Therefore, developing novel processes that are able to convert methane into value-added chemicals via oxidative catalytic reactions under mild conditions has become one of the potential solutions and is an important topic in catalysis research. However, due to the low electron/proton affinity, low polarizability, weak acidity, high C–H bond strength (439 kJ mol⁻¹), and the high ionization energy of a methane molecule, the activation of methane under mild conditions is very difficult and requires highly reactive reagents.⁶¹ Moreover, as the target oxygenate products are generally more reactive than the methane under the same conditions, obtaining a high selectivity at a relatively high conversion is still challenging. In the gas-phase reaction, only a few catalysts, such as the Na₂WO₄-Mn catalysts, have exhibited a sum of conversion and selectivity of higher than 100%.^{64,65} Recent discoveries have revealed that chemical looping and cyclic operations using Fe- and Cu-promoted zeolites as the catalysts under stepwise or isothermal conditions are effective methods to achieve high methanol selectivity and yield in the gas-phase reaction.⁶⁶ In a typical process, methane will first react with the zeolite to form CH₃-O-metal species. The adsorbed methoxy will then desorb after protonation by the steam to form methanol products. The active sites will be further regenerated in the presence of steam or oxygen under isothermal conditions or at elevated temperature. In addition to the gas-phase methane activation processes, an enzyme-catalyzed methane oxidative conversion reaction can proceed in the aqueous phase using methane monooxygenase under mild conditions. This has encouraged the investigation of catalyst development for methane conversion in water.

A number of catalytic systems have been developed in the aqueous phase to achieve highly selective methane oxidation to methanol using both H₂O₂ and O₂ as the oxidative reagents.^{67–69} Among them, bimetallic AuPd supported on an oxide support such as TiO₂ has been reported to be an active catalyst to convert methane to methanol using H₂O₂ as the oxidant under mild conditions.⁷⁰ Other oxidation byproducts include methyl hydroperoxide and formic acid as well as CO and CO₂. However, the AuPd/TiO₂ catalysts are not very selective. The methanol selectivities of the catalysts prepared using impregnation, deposition precipitation, and sol impregnation methods are all below 20%. Mechanistic studies revealed that the high activity of H₂O₂ is the major reason for the overoxidation. When H₂ and O₂ are used as feedstocks to form H₂O₂ in the aqueous phase, the selectivity to methanol can increase significantly to 70%. Later on, using well dispersed AuPd colloidal particles in the aqueous phase as the catalyst, the

methanol selectivity was further improved to 92%.⁷¹ The intrinsic activity of the AuPd colloid catalysts reached 10.4 mol kg_{cat}⁻¹ h⁻¹, nearly 2 times higher than that of methane monooxygenase. Most recently, Xiao and co-workers have developed a novel Au-Pd bimetallic catalyst for the methane selective oxidation reaction.⁶⁹ By encapsulation of the AuPd bimetallic metal center in the hydrophobic alkyl chain modified ZSM-5, the formed H₂O₂ can be concentrated near the metal center due to the enhanced mass transfer of the nonpolar H₂/O₂ molecules and the diffusion limitation of the hydrophilic H₂O₂ through the modified zeolite. Under the optimized conditions, the methanol formation rate reached 90.6 mol kg_{cat}⁻¹ h⁻¹ with a high selectivity of 92% at 17.3% methane conversion (Figure 2b-ii).

Zeolite-bonded atomic metal catalysts are another effective group of catalysts that exhibit considerable activity in the methane partial oxidation reaction. Fe-ZSM-5 species are the most active catalysts.⁷² A detailed structural characterization and DFT calculation results suggested that the doublet [Fe₂(μ₂-OH)₂(OH)₂(H₂O)₂]²⁺ is the active site for the reaction. H₂O₂ will be activated on the Fe₂ clusters to form an •OOH radical. The major intermediate of the CH₄ activation has been identified as the methyl hydroperoxide. By release of an •OH radical, MeOOH will transform into a MeOH molecule. However, the dissociation of the O–H bond will induce the formation of formic acid or even carbon dioxide. In addition to iron-modified zeolites, Cu- and CuFe-based zeolites have also been applied in the conversion of methane to methanol.^{72–74}

Oxidative carbonylation is another potential pathway for the conversion of methane to value-added acetic acid in the aqueous phase. Traditionally, the conversion of methane to acetic acid can be performed via the transformation of methane to methanol followed by a carbonylation process with homogeneous catalysts (for example, the noble-metal-promoted Ir carbonyl complex).⁷⁵ Recently, Flytzani-Stephanopoulos et al. have reported that Rh single atoms immobilized on the ZSM-5 zeolite were able to catalyze the oxidative carbonylation of methane directly into acetic acid in the presence of CO and oxygen in a one-pot process operating in the aqueous phase.⁶⁷ Under the optimized conditions, about 22 mol kg_{cat}⁻¹ of CH₃COOH and 0.23 mol kg_{cat}⁻¹ of CH₃OH were produced in a 3 h reaction, with a selectivity of 60–100%. The reaction probably occurs with the formation of M-CH₃ species and CO and/or oxygen insertion and ends up with hydrolysis regeneration steps (Figure 2b-iii). Following a similar strategy, Ma et al. using Ir clusters as the catalyst also managed to convert ethane to acetic acid and C₃ carboxylic acid in the presence of both O₂ and CO with high chemoselectivity (70% for acetic acid) and yield in aqueous solution.⁷⁶ The high coverage of CO on the metallic clusters played a crucial role in maintaining the good selectivity to the oxygenate species.

Due to the difficulty in activating methane under mild conditions, photocatalytic conversion processes have been investigated in water. Using H₂O₂ as the oxidant, Tang et al. have reported FeOOH/Fe₂O₃-promoted TiO₂ to be a selective catalyst for the methane partial oxidation.⁷⁷ The average methanol formation rate reaches 0.345 mol kg_{cat}⁻¹ h⁻¹. The good catalytic performance is attributed to the effective electron separation at the Fe–Ti interface and the low oxygen reduction overpotentials of the catalysts. Recently, Au-based catalysts were reported to be efficient in the methane to methanol partial oxidation reaction using dioxygen as the photocatalyst. Ye et al. reported a 0.1 wt % Au promoted ZnO system.³³ The

photocatalyst was reported to transform methane and O₂ to •CH₃ and •OOH radicals in the aqueous medium, and the excess amount of water suppresses the overoxidation of generated methanol to CO₂. The methanol formation rate reached 12.5 mol kg_{cat}⁻¹ h⁻¹. A nanosheet of black phosphorus supported Au single atoms activates the methane to -CH₃ species.¹⁷ Black phosphorus was oxidized in O₂ to form surface P=O and P-O-P species, which facilitate the oxidation of CH₃ by the OH radicals originating from water. In this sense, water also works as the cocatalyst for the methane oxidation process.

Previous catalytic development has demonstrated that the aqueous phase is a suitable reaction medium for one-step methane oxidation to liquid organic compounds. One of the reasons for the improvement in selectivity on partial oxidation in the aqueous phase is probably due to the existing surface hydroxyl group that may inhibit the dissociation of O₂ and the subsequent oxidative dehydrogenation of the methoxy group.¹⁶ The aqueous phase effectively stabilizing and assisting in the formation of the highly reactive •OOH/•OH radicals is another explanation for the superior performances of the catalysts in water. However, the role water plays in the methane activation is still not clear. More experimental and theoretical efforts are required to unravel this important problem.

3.3. Aqueous-Phase Fischer–Tropsch Synthesis Reaction

Fischer–Tropsch synthesis (FTS) is a catalytic reaction that converts syngas (a mixture of CO and H₂) to hydrocarbons and valuable oxygenate chemicals.⁷⁸ Industrialized in the early 20th century, FTS has been used as a reaction process for transforming coals into liquid fuels. The FTS reaction can be catalyzed using Fe, Co, and Ru transition-metal-based materials. Traditionally, the iron-based catalysts are mainly operated in a slurry-fluid-bed reactor using a high-melting-point oil and wax as the reaction medium.⁷⁹ However, the supported cobalt-based catalysts¹⁶ are generally operated in a fixed-bed reactor.⁸⁰ It has been widely found that the water produced and cofed with the syngas reactants has a significant effect (either positive or negative) on the activity, selectivity, and stability of the FTS process (Figure 2c).^{81,82} What kind of catalytic performance will appear when the steam further converts into condensed water is an interesting topic for FT synthesis. In the past two decades, numerous experimental and theoretical studies have been performed in this area.

Kou et al. managed to synthesize a well-dispersed Ru colloid stabilized by polyvinylpyrrolidone (PVP) in the aqueous phase as the FTS catalyst.⁸³ The freestanding Ru NPs achieved a high turnover frequency (TOF) of 12.9 mol_{CO} mol_{Ru}⁻¹ h⁻¹ at only 150 °C, which is more than 1 order higher than that for the supported Ru/SiO₂ catalysts working at 200 °C in a traditional fixed-bed reactor. The promotion effect of the aqueous phase was pronounced. The activity of Ru NPs working in the aqueous phase was about 20 and 10 times higher than those in the alcohol phase and organic solvents (1,4-dioxane and cyclohexane). Despite the significant promotion effect on the catalytic activity, the aqueous-phase reaction exhibits little influence on the chain distribution of hydrocarbon products. The performance of Ru NPs in the aqueous-phase FTS reaction shows some structural sensitivity. The 2.0 nm diameter Ru particles have been identified as the most active catalysts. Smaller and larger particles are less active, which is probably due to the inability to form the B₅ active sites on NPs smaller than 2 nm and the gradually reduced surface density of B₅ sites on larger NPs. Later on, Ma and co-workers reported that the face-centered-cubic

(FCC) structured Ru particles expose even an higher density of B₅-like active sites per unit surface area in comparison to the thermodynamically stable hexagonal Ru NPs.⁸⁴ The increase in active sites was sufficient to compensate for the loss of intrinsic activity at the active sites on the FCC Ru NPs. The FTS activity of the FCC Ru NPs is 37.8 mol_{CO} mol_{Ru}⁻¹ h⁻¹ at 160 °C, which is 3 times higher than those for the most active HCP Ru NPs. Liquid-phase soluble ions,⁸⁵ capping agents,⁸⁶ and a polymer stabilizer dissolved in the aqueous phase have also been reported to tune the activity of Ru FTS catalysts.^{85,87} Among all of the tested promoters, Cl⁻, CO₃²⁻, and TTAB were reported to enhance the FTS activity.⁸⁵ These anionic and organic promoters can only functionalize in the liquid-phase reaction, which enriched the mechanistic understanding of aqueous-phase FTS catalysts. Additionally, unprecedented selectivity to oxygenate products has been observed over the NaBH₄-reduced Ru NP catalysts in the aqueous FTS.⁸⁸ Although the reaction rate over the Ru NPs synthesized in this way is much lower in comparison with that over H₂-reduced Ru NPs, the selectivity of alcohol and aldehyde is up to 66% in the CO₂-free products (aldehyde/alcohol ratio over 10), which has rarely been discovered in Ru-based FTS catalytic systems.⁸⁸ The relatively high CO termination rate in comparison with the low CO dissociation rate on the small Ru particles' lack of step sites was attributed to be the reason for the high oxygenate selectivity. The stability of quasi-homogeneous Ru NPs in an aqueous solution at elevated temperature was evaluated using a continuous-flow autoclave reactor and scale-up to the 1 L level.⁸⁹ The stabilizer/metal ratio has been reported to be the major factor that determines the stability of the catalysts. Under the optimized conditions, the CO conversion of the system remains relatively stable for over 240 h, achieving a C₅₊ product yield of 0.51 g g_{cat}⁻¹ h⁻¹ at 150 °C. This work verified the potential of aqueous FTS in syngas conversion. In addition to the freestanding colloidal Ru NPs, the supported Ru-based catalysts also exhibited competitive activity in the aqueous-phase FT synthesis. Cases include Ru/TiO₂ and Ru/carbon nanofiber.^{90,91}

In comparison with ruthenium, reduced 3d metals particles are less stable under hydrothermal conditions. So far, only Co-based catalysts have been developed for aqueous-phase reaction and a few Fe AFTS catalysts have been reported.^{87,92} Ma et al. developed Pt-modified Co NPs stabilized by PVP for the aqueous-phase FTS reaction.⁹³ The added 10% of Pt was identified to be mainly located at the sublayer of the Co NPs and modulated the activity and selectivity of the Co overlayer. The activity of the catalysts was determined to be above 1.0 h⁻¹ at 160 °C with a C₅₊ hydrocarbon selectivity of over 70%. Davis et al. also found that the Pt-promoted Co/Al₂O₃ catalysts exhibited higher CO conversion rates in comparison to the unpromoted catalysts in aqueous solution.⁹⁴ However, the activities of catalysts in the aqueous phase are similar to those in an organic medium.

Due to the lack of effective characterization methods dealing with a solid–liquid interface, the function of the aqueous phase in promoting the FTS catalyst performance is still experimentally unclear. However, kinetic studies and an investigation of the function of steam in the traditional gas–solid interface provide useful information on this topic. For the enhanced activity, one possible explanation for the high FTS rate at low temperature in water is the H-shuttling effect (Figure 2c-ii). The water accommodates adsorbed H as the acceptor and facilitates the H-assisted dissociation of CO, the rate-limiting step of the

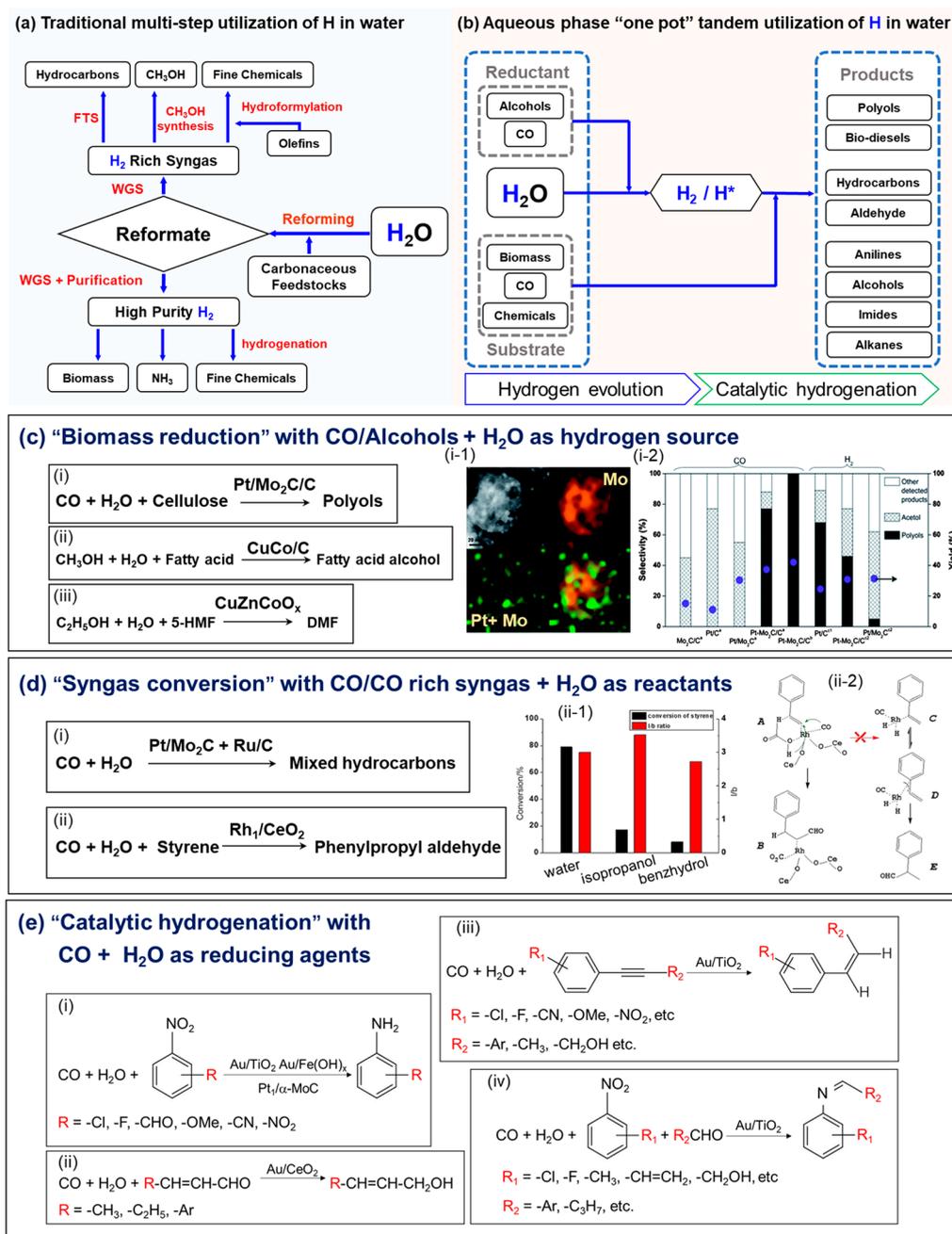


Figure 3. Schematic comparison of traditional (a) and new processes (b) in heterogeneous catalysis for utilization of hydrogen in water in catalytic hydrogenation reactions. (c) The conversion of biomass with H₂O and CO/alcohols as reductants (example reactions (i)–(iii): (i-1) and (i-2) bifunctional Pt/Mo₂C-Pt/C catalyst and its excellent performance for cellulose hydrogenation to polyols).²⁶ (d) The catalytic conversion of CO and H₂O to mixed hydrocarbons and chemicals via synthesis gas reactions (example reactions (i) and (ii), Fischer–Tropsch synthesis and hydroformylation reactions; (ii-1) and (ii-2) catalytic performance of single-atom Rh catalysts in water and reaction mechanism in an aqueous-phase hydroformylation reaction using CO and H₂O as reactants).¹⁰⁷ (e) Chemoselective hydrogenation and hydrofunctionalization reactions using H₂O and CO as reactants (example reactions (i)–(iv)).

FTS reaction.⁹⁵ The aqueous phase also prolongs the residence time of water on the surface in comparison with steam in the gas feed, which explains its superiority in promoting the activity of FTS catalysts. The dense water molecules in the aqueous phase enhance the CO coverage, which may enhance the probability of the CO termination step, leading to an enhanced oxygenate selectivity (Figure 2c-iii).^{96,97}

4. NEW HETEROGENEOUS PROCESSES ACHIEVED IN THE AQUEOUS PHASE

In this part we will focus on the recently developed new heterogeneous processes in the aqueous phase where water works as the reactant in addition to its role as the reaction medium and catalyst promoter, especially in hydrogenation reactions employing the *in situ* generated hydrogen from water as the H source under moderate conditions. In the traditional conversion routes, the generation of hydrogen and the

utilization of the generated H₂ are performed separately via carbonaceous feedstock reforming and different syngas procedures and hydrogenation reactions in different specially designed reactors (Figure 3a). The participation of the aqueous phase is able to couple the hydrogen generation and utilization together in a one-pot tandem strategy (Figure 3b). The exploitation of these new chemical processes generally requires the existence of hydrogen evolution active sites (alcohol reforming or water-gas shift active sites, for example) in the catalyst, which provides considerable promotion in comparison with the traditional hydrogenation processes in biomass reduction, syngas processes, and fine chemical hydrogenation reactions, including activity, selectivity, and poisoning resistance.

4.1. Conversion of Biomass Using H₂O as the Hydrogen Source

The catalytic refinement of lignocellulose is an important and potential method to convert regenerable biomass products into value-added chemicals. Typically, the catalytic hydrogenation of cellulosic biomass directly into polyols in the aqueous phase is one of the commonly used protocols for the synthesis of platform molecules.^{98,99} The key factor lies in the selectivity control of hydrolysis and cleavage of specific C–C and/or C–O bonds.^{100–102} The use of high-pressure hydrogen benefits the mass transport of hydrogen in the water due to its low solubility for biomass and enhances the transformation rate. However, the use of high-pressure pure hydrogen is costly, especially for distributed biomass conversion facilities. Finding high pressure H₂ free biomass hydrogenation processes by using the H in the water as the hydrogen source is highly desirable.

The water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) is one of the applicable *in situ* hydrogen production processes. In a pioneering research work, Li et al. reported the direct conversion of cellulose using CO and H₂O on a Pt–Mo₂C catalyst derived from a carbon thermal reduction method (Figure 3c-i).²⁶ A detailed structure analysis demonstrated that Pt/molybdenum carbide and Pt/C active phases coexisted in the catalyst. Different from the results of conventional Pt/C-catalyzed hydrogenation/hydrogenolysis of cellulose with high-pressure H₂ (3.7 MPa) as the reductant, the yield of polyols was almost doubled with a sorbitol selectivity of up to ~100% for Pt–Mo₂C/C using CO and H₂O as the hydrogen source. The coexistence of two different active sites in the Pt/Mo₂C/C catalyst was proposed to be the reason for the excellent performance. The Pt–Mo₂C domain is responsible for the formation of reactive hydrogen species, while Pt/C serves as the site for the consequent cellulose hydrogenation. The relatively higher solubility of CO in the aqueous phase and the highly efficient WGS reaction that converts the dissolved CO into active H/H₂ account for the improved hydrogenation rate of the CO–water–Pt system. More interestingly, the yield of polyol products is relatively independent of CO partial pressure over Pt/Mo₂C/C catalysts. This phenomenon suggests that it is possible to develop a low-pressure biomass hydrogenation to polyols process based on the Pt/Mo₂C/C catalyst.

In addition to CO, organic compounds have also been studied as the reductants to manufacture hydrogen *in situ* from an aqueous phase for the H₂-free biomass hydrogenation reactions. The pertinent biomass conversion reactions include a fatty acid upgrade to a fatty alcohol, 5-HMF hydrogenation, etc.^{103,104} However, the organic reductants are generally biomass-derived small molecules such as C_{1–3} alcohols and formic acid. In these

reactions, the hydrogen can be fully generated from the organic hydrogen source dehydrogenation/decomposition reactions (such as methanol decomposition, isopropanol dehydrogenation) or partially from water using the aqueous reforming reactions discussed in section 3. In comparison with the former route, the APR route can activate the H from water and make full use of the organic sacrificial reagents. However, the tandem reaction of the APR of organic alcohols and biomass hydrogenation generally requires harsher conditions. Due to the mismatch of the suitable conditions of APR of alcohols and the hydrogenation processes as well as the potential esterification and etherification between the biomass functional groups and the excess amount of liquid hydrogen sources, the product selectivity is usually worse than that for a direct hydrogenation using dihydrogen as the reductant.^{105,106}

4.2. Catalytic Conversion of CO and H₂O to Mixed Hydrocarbons and Chemicals

As discussed in section 3.3, the aqueous-phase FTS (APFTS) could effectively reduce the reaction temperature and improve the equilibrium conversion rate of CO with pronounced activity. Most noteworthy is the APFTS reaction that leads to the production of liquid fuels with high selectivity under mild conditions, especially when ruthenium-based catalysts are used.

On the basis of the advantages of the APFTS reaction by the promoting effect of water as a mediator, Ma's group further proposed a new strategy to couple the WGS reaction and FTS in the aqueous phase, in which liquid fuels could be generated directly from CO and H₂O without adding the synthesis gas at a specific H₂:CO ratio.²⁵ The construction of a highly efficient Pt–Mo₂C/C + Ru/C combination can directly convert CO and H₂O into a synthesis gas and CO₂ mixture and then to liquid hydrocarbons via a tandem WGS + FTS pathway. The hydrocarbon formation rate of the mixed catalysts is up to 8.7 mol_{–CH₂–} mol_{Ru}^{–1} h^{–1}, and the C₅₊ hydrocarbon selectivity reaches 68.4% at 200 °C, which are comparable to those of the conventional APFTS process using synthesis gas as reactant.

In addition to the Fischer–Tropsch synthesis, CO + H₂O can also be applied in the hydroformylation reaction. Li et al. reported the hydroformylation of styrene with CO and *in situ* hydrogen generated from CO WGS reactions on a Rh single-atom catalyst (Figure 3d-i).¹⁰⁷ Different from those heterogeneous hydroformylation catalysts with high branched aldehyde selectivity, Rh₁/CeO₂ exhibits a strong chemoselectivity (~73%) to the linear aldehydes. Detailed studies revealed that the hydrogen generated *in situ* from the water-gas shift reaction is critical to obtaining a high regioselectivity of the linear products (Figure 3d-ii).

4.3. Chemoselective Hydrogenation and Hydrofunctionalization Reaction Using H₂O and CO as Reductants

The utilization of water as the liquid hydrogen source is not limited to the reactions performed at the relatively high temperature that is the suitable condition for catalytic water-gas shift and aqueous-phase reforming reactions. In the low-temperature region, the catalytic transfer selective hydrogenation (CTH) of aniline derivatives has been achieved in the aqueous phase (Figure 3e). He et al. reported the first heterogeneous hydrogenation of nitro compounds with CO and H₂O by TiO₂-supported fine Au clusters ($\text{CO} + \text{H}_2\text{O} + \text{nitrobenzenes} \rightarrow \text{anilines} + \text{CO}_2$).¹⁰⁸ Different from the traditional understanding that the hydrogenation might proceed with the *in situ* generated H₂ from WGS, a control experiment

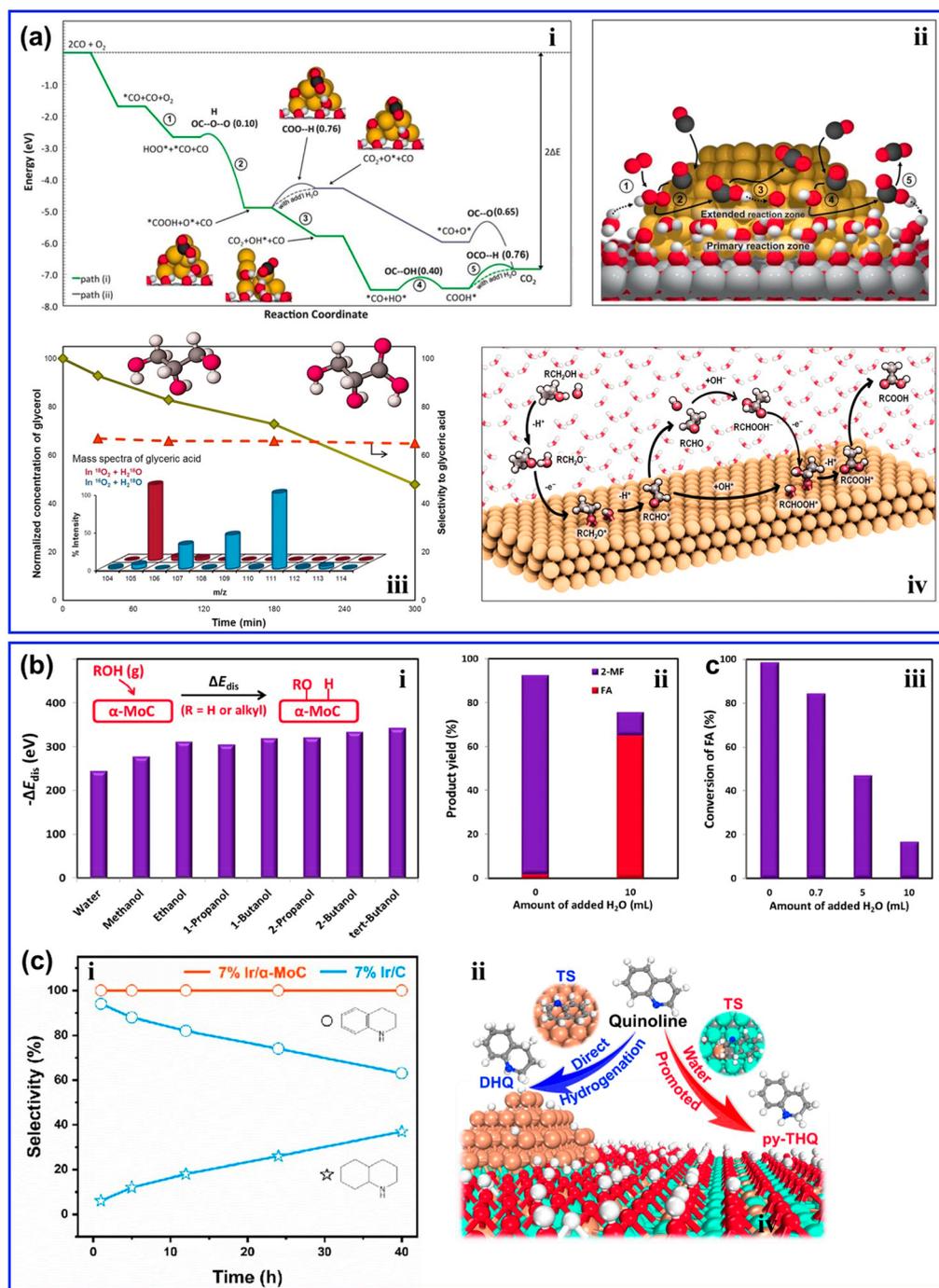


Figure 4. (a) Representative role of water as a cocatalyst for oxidation reactions in heterogeneous catalysis: ((i), (ii)) proposed reaction mechanism, potential energy diagram, and reaction pathways in catalytic CO oxidation;⁵ (iii) reaction profile for the oxidation of glycerol over Au/C in liquid water and isotopic water; (iv) reaction scheme for the oxidation of alcohols to acids over a gold surface in water at high pH. Hydroxide facilitates elementary steps in alcohol oxidation both in the solution phase and at the metal–solution interface.³⁴ (b) Modulated surface properties of a catalyst by water dissociation for selective hydrogenation reactions: (i) DFT-derived dissociative adsorption energies (ΔE_{dis}) for C1–C4 alcohols and H₂O on α -MoC(111) surfaces; effects of added H₂O on (ii) product yields of furfural hydrogenation and (iii) conversions of furfuryl alcohol on α -MoC catalysts (FA for furfuryl alcohol, 2-MF for 2-methylfuran).¹²⁷ (c) Water-promoted selective hydrogenation of quinoline in the aqueous phase.¹²⁸

with H₂ as the reductant showed no conversion of substrates. The reasonable mechanism was that CO-induced reduction of H₂O promoted the formation of transient Au–H species, and the hydrogen-delivery rate was higher than those for conventional Au-catalyzed hydrogenation processes. More interestingly, the reduction of a series of structurally diverse nitro compounds are all selective to the corresponding amino

aromatics, regardless of the presence of $-C=C$, $-C\equiv N$, and $-C=O$ groups or dinitrobenzenes.^{109–115} Despite the excellent selectivity of Au(vs)/TiO₂, the transformation rate of this system is relatively limited. At low conversion, the average turnover frequency is only $\sim 100\text{ h}^{-1}$, which might be due to the inability of the Au based-catalyst to form the unstable Au–H species.

Later on, Lin et al. improved the nitroaromatic reduction activity using CO and H₂O as the hydrogen source with atomically dispersed Pt on an α -MoC support as the catalyst.²⁸ For the hydrogenation of nitrobenzenes, Pt₁/ α -MoC shows 99% chemoselectivity with 100% conversion of substrates, with a more than 1 order of magnitude higher TOF (3500 h⁻¹) in comparison to the aforementioned Au/TiO₂ catalyst. For comparison, the commercial Pt/C catalyst and Pt₁/FeO_x show negligible activities. The catalyst exhibits good chemoselectivity to the nitro-group reduction even in the presence of other vulnerable functional groups such as $-C=C$, $-C\equiv C$, $-C=O$, etc. The excellent anti-CO-poisoning hydrogenation ability of the Pt-based catalyst is different from that of the Au/TiO₂ catalyst from a mechanistic point of view. In the reaction, the nitrobenzene will first dissociate into a C₆H₅N* surface intermediate on the carbide support with the assistance of Pt, which prefers to be protonated by water into aniline rather than be hydrogenated by H₂/H*. However, the remaining oxygen species from water on the α -MoC will further react with adsorbed CO or dissociated hydrogen on the electron-deficient Pt atoms via a WGS-like reforming process into CO₂ and H₂O. This water protonation mechanism is the reason for the Pt/ α -MoC catalyst being able to efficiently work in the presence of concentrated CO in the aqueous phase.

In summary, the participation of water in the reduction reactions of biomass, C₁ processes, and fine chemical reduction reactions as the hydrogen source has demonstrated its potential in promoting the hydrogenation activity and selectivity. Additionally, it provides a novel pathway to turn the hydrogen-lean crude hydrogen into useful hydrogenation resources. For example, the exhaust gas of the iron and steel industries contains 70% or more CO. The processes discussed above not only remove the environmental contaminants (CO) but also generate compounds of economic interest. However, it should be noted that these processes will generate more CO₂ emission in comparison to traditional hydrogenation reactions, especially for the syngas reaction. Special note should be made with regard to the reaction selection in a consideration of the carbon efficiency. Meanwhile, the introduction of CO₂ capture techniques into these processes might be necessary to overcome this disadvantage.

5. MICROSCALE AQUEOUS ENVIRONMENT PROMOTED CATALYTIC PERFORMANCES

In the previous two sections, we focused on heterogeneous catalytic reactions in the aqueous phase. In these catalytic systems, water acts as a solvent and reaction medium first and further works as a catalyst promoter, cocatalyst, and reactant. In other traditional gas–solid reactions, the existence of water in the gas feed may cause it to be adsorbed on the catalyst and form a microscale aqueous environment on the hydrophilic/reactive substrate, which might promote the performance of the heterogeneous catalyst. In this part we will briefly summarize the typical cases in which the presence of a microscale aqueous environment around active sites could promote the activation of pivotal substrates such as O₂ and H₂O for certain reactions (Figure 4).

One of the classic cases is the activation of oxygen for CO oxidation reactions. The adsorption of a trace amount of water near the active site facilitates the activation of oxygen, which is probably one of the rate-limiting steps in oxidation reactions. In the CO oxidation or preferential oxidation of CO in H₂ (PROX), the reaction between adsorbed O₂ and water generates

active *OOH species at the interface of the noble metal and oxide support (for example, Au/TiO₂), resulting in the promotion of activity by orders of magnitude (Figure 4a-i, ii).^{5,116–119} Moreover, recent studies show the promotion effect on an oxide-supported single-atom catalyst is much more pronounced in comparison to traditional metal nanoparticle supported catalysts.^{118,120} The hydroxyl from dissociated water reacts with CO to form a highly active carboxyl intermediate, which subsequently dehydrogenates with the assistance of a lattice oxygen to generate CO₂ and water.¹²¹ Similarly, in the selective oxidation of alcohols on the supported Au catalysts, the reaction between O₂ and water produces hydrogen peroxide (HOOH*) that decomposes into hydroxide, which significantly reduces the activation barrier of O₂.^{34,122,123} The adsorbed hydroxide is effective in activating both the C–H and O–H bonds in alcohols (Figure 4a-iii, iv).

Another promoting effect of microscale water was the modulated surface properties of catalyst by water dissociation. In the water-gas shift reaction over α -MoC-based catalysts, it has been discovered that the dissociated species of water (O* or hydroxyl) can adsorb on the surface of the carbide.^{124–126} These species can form a strong hydrogen-bond network on the surface, which enhances the further dissociation of water and accelerates the proton transportation. This effect is one of the main reasons for the extraordinary low-temperature activity of metal/ α -MoC catalysts in the WGS reaction. Additionally, the O/OH/H species originating from water on the active sites change the adsorption or readsorption behavior of the substrates or products, resulting in distinct differences in the activities and selectivities of products. For example, for the hydrogenation of bio-derived furfural and quinoline on α -MoC-based catalysts, the efficient splitting of water and strong bonding with the generated hydroxide species promoted the desorption of semihydrogenated products such as furfuryl alcohol (Figure 4b) and 1,2,3,4-tetrahydroquinoline (Figure 4c).^{127,128}

6. OUTLOOK AND PERSPECTIVES

In summary, the previous studies of heterogeneous catalytic systems in the aqueous phase have demonstrated that water is more than a simple reaction medium. The positive effect of the water phase includes but is not limited to the following: (a) a catalytic performance promotion effect by influencing the thermodynamics, changing the barrier of the reaction, and working as a cocatalyst to provide or stabilize the highly reactive species; (b) participating in the catalytic reaction as a hydrogen donor, enabling new processes, and enhancing the reactivity and selectivity; (c) forming a microscale aqueous environment on the surface of heterogeneous catalysts, which facilitates the transportation of hydrogen, protons, and oxygen on the solid–liquid interface and changes the adsorption behaviors of reactants for certain reactions. The existence of these constructive effects of water originates from the special physical–chemical properties of water molecules and makes the aqueous phase a promising system to promote traditional gas-phase heterogeneous catalytic reactions. Despite the current success, the development of catalytic systems is still limited and the role of water has not been well unraveled yet on the basis of direct experimental evidence. The catalytic stability in water, one of the critically important parameters of catalytic performance in addition to catalytic activity and selectivity, has not been systematically studied. To obtain a better understanding of the water effect and fully exploit the promotion effect of aqueous

phase reaction, more studies can be performed in the following areas.

- (1) The heterogeneous catalytic systems and reactions applicable to the aqueous phase need to be further expanded. A systematic understanding of the types of reactions that share strong or weak promotion effects from aqueous-phase reactions needs to be summarized.
- (2) The lack of suitable characterization techniques that study the structure of solid–water interfaces, especially the *in situ* techniques with high spatial and temporal resolution, limits the understanding of aqueous-phase catalytic systems. The traditional surface-sensitive probes, such as soft X-rays and low-energy electrons, are not capable of penetrating the aqueous layers due to their small mean free path. Methods to perform *in situ* experiments using a powerful scanning probe microscope are still under development.¹²⁹ Therefore, developing relevant methods to obtain experimental knowledge of the interface structure and elucidate the adsorption behaviors of water near the solid surface will enhance the understanding of heterogeneous catalysts in the aqueous phase. Surface science studies using well-defined model surfaces are also of great significance. A reflective spectroscopic method, such as infrared spectroscopy, will play an increasingly important role in this field.¹³⁰
- (3) The determination of the intrinsic activity and kinetic parameters of a heterogeneous catalytic system in the aqueous phase is difficult, as most reactions are performed in nondifferential batch reactors.¹³¹ The description of the transportation behavior of reactants and products within the interface of solid catalysts and water is still a huge research challenge.¹³² As a result, the understanding of the kinetic and molecular dynamic behaviors of aqueous-phase reactions are relatively limited in comparison with gas–solid reactions. Progress in these areas will significantly enhance the the understanding of the mechanism of the heterogeneous catalysis in an aqueous phase.
- (4) The theoretical study of the heterogeneous reaction in the aqueous phase is difficult, and the calculation expense of the reaction process remains relatively high. To optimize a solid–water reaction system well and further simulate the catalytic reaction, the chemical properties of four distinct regions need to be studied: namely, the bulk aqueous phase, the electric double layer, the solid interface, and the subsurface of the catalyst. The combination of different methods and tools including empirical molecular mechanics and *ab initio* methods are needed to simulate a heterogeneous catalytic reaction in water well.¹³³ New methods and theoretical approaches are highly desirable to obtain a molecular level understanding of aqueous-phase reactions and the rational design of the corresponding catalytic systems.
- (5) Despite the positive effects of aqueous-phase reactions, an aqueous-phase reaction at elevated temperature is a huge challenge for the stability of heterogeneous catalysts, especially for the 3d metal, zeolite and MOF based catalysts, due to the redox corrosion, the leaching of Si and Al by the aqueous medium, and the framework damage caused by ligand substitution of water and hydroxyl species.¹³⁴ In order to fully exploit the advantages of aqueous-phase catalytic reactions, developing highly

stable catalysts and exploring methods to effectively prolong the lifetime of heterogeneous catalysts in water are of great importance, especially for the potential use of aqueous-phase catalytic reactions in the industrial scenario. Recent studies using a hydrophobic material coating¹³⁵ and the fully encapsulated “chain-mail catalysts”¹³⁶ are effective attempts toward this target.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Xu, Y.; Li, X.; Gao, J.; Wang, J.; Ma, G.; Wen, X.; Yang, Y.; Li, Y.; Ding, M. A hydrophobic FeMn@Si catalyst increases olefins from syngas by suppressing C1 by-products. *Science* **2021**, *371* (6529), 610–613.

- (2) Ohtsuka, H.; Tabata, T. Effect of water vapor on the deactivation of Pd-zeolite catalysts for selective catalytic reduction of nitrogen monoxide by methane. *Appl. Catal., B* **1999**, *21* (2), 133–139.
- (3) Zhang, X.; Zhang, M.; Deng, Y.; Xu, M.; Artiglia, L.; Wen, W.; Gao, R.; Chen, B.; Yao, S.; Zhang, X.; Peng, M.; Yan, J.; Li, A.; Jiang, Z.; Gao, X.; Cao, S.; Yang, C.; Kropf, A. J.; Shi, J.; Xie, J.; Bi, M.; van Bokhoven, J. A.; Li, Y. W.; Wen, X.; Flytzani-Stephanopoulos, M.; Shi, C.; Zhou, W.; Ma, D. A stable low-temperature H₂-production catalyst by crowding Pt on alpha-MoC. *Nature* **2021**, *589* (7842), 396–401.
- (4) Li, G.; Wang, B.; Resasco, D. E. Water-mediated heterogeneously catalyzed reactions. *ACS Catal.* **2020**, *10* (2), 1294–1309.
- (5) Saavedra, J.; Doan, H. A.; Pursell, C. J.; Grabow, L. C.; Chandler, B. D. The critical role of water at the gold-titania interface in catalytic CO oxidation. *Science* **2014**, *345* (6204), 1599–602.
- (6) Croft, G.; Fuller, M. J. Water-promoted oxidation of carbon monoxide over tin(IV) oxide-supported palladium. *Nature* **1977**, *269* (5629), 585–586.
- (7) Anastas, P.; Eghbali, N. Green chemistry: principles and practice. *Chem. Soc. Rev.* **2010**, *39* (1), 301–312.
- (8) Haumann, M.; Koch, H.; Hugo, P.; Schomäcker, R. Hydroformylation of 1-dodecene using Rh-TPPTS in a microemulsion. *Appl. Catal., A* **2002**, *225* (1–2), 239–249.
- (9) Gedye, G. R. Effect of water as a promoter of chemical reactions. *Sci. Prog. (1919-1933)* **1929**, *24* (90), 248–262.
- (10) Cicco, L.; Sblendorio, S.; Mansueto, R.; Perna, F. M.; Salomone, A.; Florio, S.; Capriati, V. Water opens the door to organolithiums and Grignard reagents: exploring and comparing the reactivity of highly polar organometallic compounds in unconventional reaction media towards the synthesis of tetrahydrofurans. *Chem. Sci.* **2016**, *7* (2), 1192–1199.
- (11) Neylon, M. K.; Castagnola, M. J.; Castagnola, N. B.; Marshall, C. L. Coated bifunctional catalysts for NO_x SCR with C₃H₆. *Catal. Today* **2004**, *96* (1–2), 53–60.
- (12) Pirkanniemi, K.; Sillanpää, M. Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere* **2002**, *48* (10), 1047–1060.
- (13) Wang, Z.; van Oers, M. C. M.; Rutjes, F. P. J. T.; van Hest, J. C. M. Polymersome colloidosomes for enzyme catalysis in a biphasic system. *Angew. Chem.* **2012**, *124* (43), 10904–10908.
- (14) Pera-Titus, M.; Leclercq, L.; Clacens, J. M.; De Campo, F.; Nardello-Rataj, V. Pickering interfacial catalysis for biphasic systems: from emulsion design to green reactions. *Angew. Chem., Int. Ed.* **2015**, *54* (7), 2006–2021.
- (15) Adams, J. S.; Chemburkar, A.; Priyadarshini, P.; Ricciardulli, T.; Lu, Y.; Maliekkal, V.; Sampath, A.; Winikoff, S.; Karim, A. M.; Neurock, M.; Flaherty, D. W. Solvent molecules form surface redox mediators in situ and cocatalyze O₂ reduction on Pd. *Science* **2021**, *371* (6529), 626–632.
- (16) Liu, Z.; Huang, E.; Orozco, I.; Liao, W.; Palomino, R. M.; Rui, N.; Duchon, T.; Nemsak, S.; Grinter, D. C.; Mahapatra, M.; Liu, P.; Rodriguez, J. A.; Senanayake, S. D. Water-promoted interfacial pathways in methane oxidation to methanol on a CeO₂-Cu₂O catalyst. *Science* **2020**, *368* (6490), 513–517.
- (17) Luo, L.; Luo, J.; Li, H.; Ren, F.; Zhang, Y.; Liu, A.; Li, W. X.; Zeng, J. Water enables mild oxidation of methane to methanol on gold single-atom catalysts. *Nat. Commun.* **2021**, *12* (1), 1218.
- (18) Tomita, K.; Koda, S.; Oshima, Y. Catalytic hydration of propylene with MoO₃/Al₂O₃ in supercritical water. *Ind. Eng. Chem. Res.* **2002**, *41* (14), 3341–3344.
- (19) Manabe, K.; Iimura, S.; Sun, X. M.; Kobayashi, S. Dehydration reactions in water. Bronsted Acid-surfactant-combined catalyst for ester, ether, thioether, and dithioacetal formation in water. *J. Am. Chem. Soc.* **2002**, *124* (40), 11971–11978.
- (20) Stanciakova, K.; Weckhuysen, B. M. Water-active site interactions in zeolites and their relevance in catalysis. *Trends Chem.* **2021**, *3* (6), 456–468.
- (21) Liu, Y.; Vjunov, A.; Shi, H.; Eckstein, S.; Camaioni, D. M.; Mei, D.; Barath, E.; Lercher, J. A. Enhancing the catalytic activity of hydronium ions through constrained environments. *Nat. Commun.* **2017**, *8*, 14113.
- (22) Sushkevich, V. L.; Kots, P. A.; Kolyagin, Y. G.; Yakimov, A. V.; Marikutsa, A. V.; Ivanova, I. I. Origin of water-induced Bronsted acid sites in Sn-BEA zeolites. *J. Phys. Chem. C* **2019**, *123* (9), 5540–5548.
- (23) Nakajima, K.; Baba, Y.; Noma, R.; Kitano, M.; Kondo, J. N.; Hayashi, S.; Hara, M. Nb₂O₅·nH₂O as a heterogeneous catalyst with water-tolerant Lewis acid sites. *J. Am. Chem. Soc.* **2011**, *133* (12), 4224–4227.
- (24) Zhang, K.; Suh, J. M.; Choi, J. W.; Jang, H. W.; Shokouhimehr, M.; Varma, R. S. Recent advances in the nanocatalysts-assisted NaBH₄ reduction of nitroaromatics in water. *ACS Omega* **2019**, *4* (1), 483–495.
- (25) Xu, Y.; Li, J.; Li, W.; Li, W.; Zhang, X.; Zhao, Y.; Xie, J.; Wang, X.; Liu, X.; Li, Y.; Xiao, D.; Yin, Z.; Cao, Y.; Ma, D. Direct conversion of CO and H₂O into liquid fuels under mild conditions. *Nat. Commun.* **2019**, *10* (1), 1389.
- (26) Li, J.; Liu, L.; Liu, Y.; Li, M.; Zhu, Y.; Liu, H.; Kou, Y.; Zhang, J.; Han, Y.; Ma, D. Direct conversion of cellulose using carbon monoxide and water on a Pt–Mo₂C/C catalyst. *Energy Environ. Sci.* **2014**, *7* (1), 393–398.
- (27) Xiang, Y.; Li, X.; Lu, C.; Ma, L.; Yuan, J.; Feng, F. Reaction performance of hydrogen from aqueous-phase reforming of methanol or ethanol in hydrogenation of phenol. *Ind. Eng. Chem. Res.* **2011**, *50* (6), 3139–3144.
- (28) Lin, L.; Yao, S.; Gao, R.; Liang, X.; Yu, Q.; Deng, Y.; Liu, J.; Peng, M.; Jiang, Z.; Li, S.; Li, Y. W.; Wen, X. D.; Zhou, W.; Ma, D. A highly CO-tolerant atomically dispersed Pt catalyst for chemoselective hydrogenation. *Nat. Nanotechnol.* **2019**, *14* (4), 354–361.
- (29) Zhai, Q.; Xie, S.; Fan, W.; Zhang, Q.; Wang, Y.; Deng, W.; Wang, Y. Photocatalytic conversion of carbon dioxide with water into methane: Platinum and copper(I) oxide co-catalysts with a core-shell structure. *Angew. Chem.* **2013**, *125* (22), 5888–5891.
- (30) Wang, Y.; Shang, X.; Shen, J.; Zhang, Z.; Wang, D.; Lin, J.; Wu, J. C. S.; Fu, X.; Wang, X.; Li, C. Direct and indirect Z-scheme heterostructure-coupled photosystem enabling cooperation of CO₂ reduction and H₂O oxidation. *Nat. Commun.* **2020**, *11* (1), 3043.
- (31) Anpo, M.; Yamashita, H.; Ichihashi, Y.; Fujii, Y.; Honda, M. Photocatalytic reduction of CO₂ with H₂O on titanium oxides anchored within micropores of zeolites: Effects of the structure of the active sites and the addition of Pt. *J. Phys. Chem. B* **1997**, *101* (14), 2632–2636.
- (32) Bagherzadeh Mostaghimi, A. H.; Al-Attas, T. A.; Kibria, M. G.; Siahrostami, S. A review on electrocatalytic oxidation of methane to oxygenates. *J. Mater. Chem. A* **2020**, *8* (31), 15575–15590.
- (33) Song, H.; Meng, X.; Wang, S.; Zhou, W.; Wang, X.; Kako, T.; Ye, J. Direct and selective photocatalytic oxidation of CH₄ to oxygenates with O₂ on cocatalysts/ZnO at room temperature in water. *J. Am. Chem. Soc.* **2019**, *141* (51), 20507–20515.
- (34) Zope, B. N.; Hibbitts, D. D.; Neurock, M.; Davis, R. J. Reactivity of the gold/water interface during selective oxidation catalysis. *Science* **2010**, *330* (6000), 74–78.
- (35) Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V. The hydrogen economy. *Phys. Today* **2004**, *57* (12), 39–44.
- (36) Turner, J. A. Sustainable hydrogen production. *Science* **2004**, *305* (5686), 972–974.
- (37) Cortright, R. D.; Davda, R. R.; Dumesic, J. A. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* **2002**, *418* (6901), 964–967.
- (38) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. Raney Ni-Sn catalyst for H₂ production from biomass-derived hydrocarbons. *Science* **2003**, *300* (5628), 2075–2077.
- (39) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew. Chem., Int. Ed.* **2007**, *46* (38), 7164–7183.
- (40) Davda, R. R.; Dumesic, J. A. Catalytic reforming of oxygenated hydrocarbons for hydrogen with low levels of carbon monoxide. *Angew. Chem., Int. Ed.* **2003**, *42* (34), 4068–4071.

- (41) Ogden, J. M. Prospects for building a hydrogen energy infrastructure. *Annu. Rev. Energy* **1999**, *24* (1), 227–279.
- (42) U.S. Department of Energy Hydrogen, Fuel Cells and Infrastructure Technologies Program, Hydrogen Posture Plan, 2006.
- (43) Lindström, B. Hydrogen generation by steam reforming of methanol over copper-based catalysts for fuel cell applications. *Int. J. Hydrogen Energy* **2001**, *26* (9), 923–933.
- (44) Liguras, D. K.; Kondarides, D. I.; Verykios, X. E. Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts. *Appl. Catal., B* **2003**, *43* (4), 345–354.
- (45) Mattos, L. V.; Jacobs, G.; Davis, B. H.; Noronha, F. B. Production of hydrogen from ethanol: review of reaction mechanism and catalyst deactivation. *Chem. Rev.* **2012**, *112* (7), 4094–4123.
- (46) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H. J.; Junge, H.; Gladiali, S.; Beller, M. Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide. *Nature* **2013**, *495* (7439), 85–89.
- (47) Ciftci, A.; Lighthart, D. A. J. M.; Sen, A. O.; van Hoof, A. J. F.; Friedrich, H.; Hensen, E. J. M. Pt-Re synergy in aqueous-phase reforming of glycerol and the water–gas shift reaction. *J. Catal.* **2014**, *311*, 88–101.
- (48) Elliott, D. C.; Sealock, L. J. Aqueous catalyst systems for the water-gas shift reaction. 1. Comparative catalyst studies. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22* (3), 426–431.
- (49) Lin, L.; Zhou, W.; Gao, R.; Yao, S.; Zhang, X.; Xu, W.; Zheng, S.; Jiang, Z.; Yu, Q.; Li, Y. W.; Shi, C.; Wen, X. D.; Ma, D. Low-temperature hydrogen production from water and methanol using Pt/alpha-MoC catalysts. *Nature* **2017**, *544* (7648), 80–83.
- (50) Davda, R. R.; Shabaker, J. W.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts. *Appl. Catal., B* **2005**, *56* (1–2), 171–186.
- (51) Yongfeng, L. Effects of ZrO₂-promoter on catalytic performance of CuZnAlO catalysts for production of hydrogen by steam reforming of methanol. *Int. J. Hydrogen Energy* **2004**, *29* (15), 1617–1621.
- (52) Papavasiliou, J.; Avgouropoulos, G.; Ioannides, T. Steam reforming of methanol over copper-manganese spinel oxide catalysts. *Catal. Commun.* **2005**, *6* (7), 497–501.
- (53) Sá, S.; Silva, H.; Brandão, L.; Sousa, J. M.; Mendes, A. Catalysts for methanol steam reforming—A review. *Appl. Catal., B* **2010**, *99* (1–2), 43–57.
- (54) Ranjekar, A. M.; Yadav, G. D. Steam reforming of methanol for hydrogen production: a critical analysis of catalysis, processes, and scope. *Ind. Eng. Chem. Res.* **2021**, *60* (1), 89–113.
- (55) Lin, L.; Yu, Q.; Peng, M.; Li, A.; Yao, S.; Tian, S.; Liu, X.; Li, A.; Jiang, Z.; Gao, R.; Han, X.; Li, Y. W.; Wen, X. D.; Zhou, W.; Ma, D. Atomically dispersed Ni/alpha-MoC catalyst for hydrogen production from methanol/water. *J. Am. Chem. Soc.* **2021**, *143* (1), 309–317.
- (56) Cheng, C. K.; Foo, S. Y.; Adesina, A. A. H₂-rich synthesis gas production over Co/Al₂O₃ catalyst via glycerol steam reforming. *Catal. Commun.* **2010**, *12* (4), 292–298.
- (57) Dosso, L. A.; Vera, C. R.; Grau, J. M. Aqueous phase reforming of polyols from glucose degradation by reaction over Pt/alumina catalysts modified by Ni or Co. *Int. J. Hydrogen Energy* **2017**, *42* (30), 18853–18864.
- (58) Davda, R. R.; Shabaker, J. W.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. Aqueous-phase reforming of ethylene glycol on silica-supported metal catalysts. *Appl. Catal., B* **2003**, *43* (1), 13–26.
- (59) Shabaker, J. Aqueous-phase reforming of methanol and ethylene glycol over alumina-supported platinum catalysts. *J. Catal.* **2003**, *215* (2), 344–352.
- (60) Huber, G. W.; Shabaker, J. W.; Evans, S. T.; Dumesic, J. A. Aqueous-phase reforming of ethylene glycol over supported Pt and Pd bimetallic catalysts. *Appl. Catal., B* **2006**, *62* (3–4), 226–235.
- (61) Crabtree, R. H. Aspects of methane chemistry. *Chem. Rev.* **1995**, *95* (4), 987–1007.
- (62) Tang, P.; Zhu, Q.; Wu, Z.; Ma, D. Methane activation: the past and future. *Energy Environ. Sci.* **2014**, *7* (8), 2580–2591.
- (63) Caballero, A.; Perez, P. J. Methane as raw material in synthetic chemistry: the final frontier. *Chem. Soc. Rev.* **2013**, *42* (23), 8809–8820.
- (64) Ji, S.-f.; Xiao, T.-c.; Li, S.-b.; Xu, C.-z.; Hou, R.-l.; Coleman, K. S.; Green, M. L. H. The relationship between the structure and the performance of Na-W-Mn/SiO₂ catalysts for the oxidative coupling of methane. *Appl. Catal., A* **2002**, *225* (1–2), 271–284.
- (65) Ji, S. Surface WO₄ tetrahedron: the essence of the oxidative coupling of methane over M₂W₂Mn/SiO₂ catalysts. *J. Catal.* **2003**, *220* (1), 47–56.
- (66) Sushkevich, V. L.; Palagin, D.; Ranocchiaro, M.; van Bokhoven, J. A. Selective anaerobic oxidation of methane enables direct synthesis of methanol. *Science* **2017**, *356* (6337), 523–527.
- (67) Shan, J.; Li, M.; Allard, L. F.; Lee, S.; Flytzani-Stephanopoulos, M. Mild oxidation of methane to methanol or acetic acid on supported isolated rhodium catalysts. *Nature* **2017**, *551* (7682), 605–608.
- (68) Li, M.; Shan, J.; Giannakakis, G.; Ouyang, M.; Cao, S.; Lee, S.; Allard, L. F.; Flytzani-Stephanopoulos, M. Single-step selective oxidation of methane to methanol in the aqueous phase on iridium-based catalysts. *Appl. Catal., B* **2021**, *292*, 120124.
- (69) Jin, Z.; Wang, L.; Zuidema, E.; Mondal, K.; Zhang, M.; Zhang, J.; Wang, C.; Meng, X.; Yang, H.; Mesters, C.; Xiao, F. S. Hydrophobic zeolite modification for in situ peroxide formation in methane oxidation to methanol. *Science* **2020**, *367* (6474), 193–197.
- (70) Ab Rahim, M. H.; Forde, M. M.; Jenkins, R. L.; Hammond, C.; He, Q.; Dimitratos, N.; Lopez-Sanchez, J. A.; Carley, A. F.; Taylor, S. H.; Willock, D. J.; Murphy, D. M.; Kiely, C. J.; Hutchings, G. J. Oxidation of methane to methanol with hydrogen peroxide using supported gold-palladium alloy nanoparticles. *Angew. Chem., Int. Ed.* **2013**, *52* (4), 1280–1284.
- (71) Agarwal, N.; Freakley, S. J.; McVicker, R. U.; Althahban, S. M.; Dimitratos, N.; He, Q.; Morgan, D. J.; Jenkins, R. L.; Willock, D. J.; Taylor, S. H.; Kiely, C. J.; Hutchings, G. J. Aqueous Au-Pd colloids catalyze selective CH₄ oxidation to CH₃OH with O₂ under mild conditions. *Science* **2017**, *358* (6360), 223–227.
- (72) Hammond, C.; Forde, M. M.; Ab Rahim, M. H.; Thetford, A.; He, Q.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Dummer, N. F.; Murphy, D. M.; Carley, A. F.; Taylor, S. H.; Willock, D. J.; Stangland, E. E.; Kang, J.; Hagen, H.; Kiely, C. J.; Hutchings, G. J. Direct catalytic conversion of methane to methanol in an aqueous medium by using copper-promoted Fe-ZSM-5. *Angew. Chem.* **2012**, *124* (21), 5219–5223.
- (73) Himes, R. A.; Karlin, K. D. A new copper-oxo player in methane oxidation. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106* (45), 18877–18878.
- (74) Groothaert, M. H.; Smeets, P. J.; Sels, B. F.; Jacobs, P. A.; Schoonheydt, R. A. Selective oxidation of methane by the bis(mu-oxo)dicopper core stabilized on ZSM-5 and mordenite zeolites. *J. Am. Chem. Soc.* **2005**, *127* (5), 1394–1395.
- (75) Kalck, P.; Le Berre, C.; Serp, P. Recent advances in the methanol carbonylation reaction into acetic acid. *Coord. Chem. Rev.* **2020**, *402*, 213078.
- (76) Jin, R.; Peng, M.; Li, A.; Deng, Y.; Jia, Z.; Huang, F.; Ling, Y.; Yang, F.; Fu, H.; Xie, J.; Han, X.; Xiao, D.; Jiang, Z.; Liu, H.; Ma, D. Low temperature oxidation of ethane to oxygenates by oxygen over iridium-cluster catalysts. *J. Am. Chem. Soc.* **2019**, *141* (48), 18921–18925.
- (77) Xie, J.; Jin, R.; Li, A.; Bi, Y.; Ruan, Q.; Deng, Y.; Zhang, Y.; Yao, S.; Sankar, G.; Ma, D.; Tang, J. Highly selective oxidation of methane to methanol at ambient conditions by titanium dioxide-supported iron species. *Nat. Catal.* **2018**, *1* (11), 889–896.
- (78) Schulz, H. Short history and present trends of Fischer–Tropsch synthesis. *Appl. Catal., A* **1999**, *186* (1–2), 3–12.
- (79) Rao, V. U. S.; Stiegel, G. J.; Cinquegrano, G. J.; Srivastava, R. D. Iron-based catalysts for slurry-phase Fischer–Tropsch process: Technology review. *Fuel Process. Technol.* **1992**, *30* (1), 83–107.
- (80) Sadeqzadeh, M.; Hong, J.; Fongarland, P.; Curulla-Ferré, D.; Luck, F.; Bousquet, J.; Schweich, D.; Khodakov, A. Y. Mechanistic modeling of cobalt based catalyst sintering in a fixed bed reactor under different conditions of Fischer–Tropsch synthesis. *Ind. Eng. Chem. Res.* **2012**, *51* (37), 11955–11964.

- (81) Iglesia, E. Design, synthesis, and use of cobalt-based Fischer–Tropsch synthesis catalysts. *Appl. Catal., A* **1997**, *161* (1–2), 59–78.
- (82) Krishnamoorthy, S.; Tu, M.; Ojeda, M. P.; Pinna, D.; Iglesia, E. An investigation of the effects of water on rate and selectivity for the Fischer–Tropsch synthesis on cobalt-based catalysts. *J. Catal.* **2002**, *211* (2), 422–433.
- (83) Xiao, C.-x.; Cai, Z.-p.; Wang, T.; Kou, Y.; Yan, N. Aqueous-phase Fischer–Tropsch synthesis with a ruthenium nanocluster catalyst. *Angew. Chem.* **2008**, *120* (4), 758–761.
- (84) Li, W. Z.; Liu, J. X.; Gu, J.; Zhou, W.; Yao, S. Y.; Si, R.; Guo, Y.; Su, H. Y.; Yan, C. H.; Li, W. X.; Zhang, Y. W.; Ma, D. Chemical insights into the design and development of face-centered cubic ruthenium catalysts for Fischer–Tropsch synthesis. *J. Am. Chem. Soc.* **2017**, *139* (6), 2267–2276.
- (85) Wang, C.; Zhao, H.; Wang, H.; Liu, L.; Xiao, C.; Ma, D. The effects of ionic additives on the aqueous-phase Fischer–Tropsch synthesis with a ruthenium nanoparticle catalyst. *Catal. Today* **2012**, *183* (1), 143–153.
- (86) Quek, X.-Y.; Pestman, R.; van Santen, R. A.; Hensen, E. J. M. Effect of organic capping agents on ruthenium-nanoparticle-catalyzed aqueous-phase Fischer–Tropsch synthesis. *ChemCatChem* **2013**, *5* (10), 3148–3155.
- (87) Delgado, J. A.; Castellón, S.; Curulla-Ferré, D.; Claver, C.; Godard, C. Effect of pH on catalyst activity and selectivity in the aqueous Fischer–Tropsch synthesis catalyzed by cobalt nanoparticles. *Catal. Commun.* **2015**, *71*, 88–92.
- (88) Quek, X.-Y.; Guan, Y.; van Santen, R. A.; Hensen, E. J. M. Unprecedented oxygenate selectivity in aqueous-phase Fischer–Tropsch synthesis by ruthenium nanoparticles. *ChemCatChem* **2011**, *3* (11), 1735–1738.
- (89) Liu, L.; Sun, G.; Wang, C.; Yang, J.; Xiao, C.; Wang, H.; Ma, D.; Kou, Y. Aqueous phase Fischer–Tropsch synthesis in a continuous flow reactor. *Catal. Today* **2012**, *183* (1), 136–142.
- (90) Yu, J.-W.; Li, W.-Z.; Zhang, T.; Ma, D.; Zhang, Y.-W. Ruthenium nanoclusters dispersed on titania nanorods and nanoparticles as high-performance catalysts for aqueous-phase Fischer–Tropsch synthesis. *Catal. Sci. Technol.* **2016**, *6* (23), 8355–8363.
- (91) Ordonsky, V. V.; Khodakov, A. Y.; Legras, B.; Lancelot, C. Fischer–Tropsch synthesis on a ruthenium catalyst in two-phase systems: an excellent opportunity for the control of reaction rate and selectivity. *Catal. Sci. Technol.* **2014**, *4* (9), 2896–2899.
- (92) Wang, H.; Kou, Y. Aqueous-phase Fischer–Tropsch synthesis catalyzed by cobalt nanoparticles. *Chin. J. Catal.* **2013**, *34* (10), 1914–1925.
- (93) Wang, H.; Zhou, W.; Liu, J. X.; Si, R.; Sun, G.; Zhong, M. Q.; Su, H. Y.; Zhao, H. B.; Rodriguez, J. A.; Pennycook, S. J.; Idrobo, J. C.; Li, W. X.; Kou, Y.; Ma, D. Platinum-modulated cobalt nanocatalysts for low-temperature aqueous-phase Fischer–Tropsch synthesis. *J. Am. Chem. Soc.* **2013**, *135* (10), 4149–4158.
- (94) Pendyala, V. R. R.; Shafer, W. D.; Jacobs, G.; Davis, B. H. Fischer–Tropsch synthesis: effect of reaction temperature for aqueous-phase synthesis over a platinum promoted Co/alumina catalyst. *Catal. Lett.* **2014**, *144* (6), 1088–1095.
- (95) Hibbitts, D. D.; Loveless, B. T.; Neurock, M.; Iglesia, E. Mechanistic role of water on the rate and selectivity of Fischer–Tropsch synthesis on ruthenium catalysts. *Angew. Chem., Int. Ed.* **2013**, *52* (47), 12273–12278.
- (96) Shi, D.; Faria, J.; Pham, T. N.; Resasco, D. E. Enhanced activity and selectivity of Fischer–Tropsch synthesis catalysts in water/oil emulsions. *ACS Catal.* **2014**, *4* (6), 1944–1952.
- (97) Anaya, F.; Resasco, D. E. Enhanced Fischer–Tropsch synthesis rates by the combined presence of aqueous and organic media in biphasic systems. *ACS Catal.* **2020**, *10* (7), 4433–4443.
- (98) Fukuoka, A.; Dhepe, P. L. Catalytic conversion of cellulose into sugar alcohols. *Angew. Chem., Int. Ed.* **2006**, *45* (31), 5161–5163.
- (99) Yan, N.; Zhao, C.; Luo, C.; Dyson, P. J.; Liu, H.; Kou, Y. One-step conversion of cellobiose to C6-alcohols using a ruthenium nanocluster catalyst. *J. Am. Chem. Soc.* **2006**, *128* (27), 8714–8715.
- (100) Matson, T. D.; Barta, K.; Iretskii, A. V.; Ford, P. C. One-pot catalytic conversion of cellulose and of woody biomass solids to liquid fuels. *J. Am. Chem. Soc.* **2011**, *133* (35), 14090–14097.
- (101) Zhou, C. H.; Xia, X.; Lin, C. X.; Tong, D. S.; Beltramini, J. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem. Soc. Rev.* **2011**, *40* (11), 5588–5617.
- (102) Van de Vyver, S.; Geboers, J.; Jacobs, P. A.; Sels, B. F. Recent advances in the catalytic conversion of cellulose. *ChemCatChem* **2011**, *3* (1), 82–94.
- (103) Zhang, Z.; Zhou, F.; Chen, K.; Fu, J.; Lu, X.; Ouyang, P. Catalytic in situ hydrogenation of fatty acids into fatty alcohols over Cu-based catalysts with methanol in hydrothermal media. *Energy Fuels* **2017**, *31* (11), 12624–12632.
- (104) Tang, X.; Wei, J.; Ding, N.; Sun, Y.; Zeng, X.; Hu, L.; Liu, S.; Lei, T.; Lin, L. Chemoselective hydrogenation of biomass derived 5-hydroxymethylfurfural to diols: Key intermediates for sustainable chemicals, materials and fuels. *Renewable Sustainable Energy Rev.* **2017**, *77*, 287–296.
- (105) Wang, J.; Nie, R.; Xu, L.; Lyu, X.; Lu, X. Catalytic transfer hydrogenation of oleic acid to octadecanol over magnetic recoverable cobalt catalysts. *Green Chem.* **2019**, *21* (2), 314–320.
- (106) Zhang, Z.; Jing, M.; Chen, H.; Okejiri, F.; Liu, J.; Leng, Y.; Liu, H.; Song, W.; Hou, Z.; Lu, X.; Fu, J.; Liu, J. Transfer hydrogenation of fatty acids on Cu/ZrO₂: Demystifying the role of carrier structure and metal-support interface. *ACS Catal.* **2020**, *10* (16), 9098–9108.
- (107) Li, T.; Chen, F.; Lang, R.; Wang, H.; Su, Y.; Qiao, B.; Wang, A.; Zhang, T. Styrene hydroformylation with in situ hydrogen: regioselectivity control by coupling with the low-temperature water-gas shift reaction. *Angew. Chem., Int. Ed.* **2020**, *59* (19), 7430–7434.
- (108) He, L.; Wang, L.-C.; Sun, H.; Ni, J.; Cao, Y.; He, H.-Y.; Fan, K.-N. Efficient and selective room-temperature gold-catalyzed reduction of nitro compounds with CO and H₂O as the hydrogen source. *Angew. Chem.* **2009**, *121* (50), 9702–9705.
- (109) He, L.; Yu, F. J.; Lou, X. B.; Cao, Y.; He, H. Y.; Fan, K. N. A novel gold-catalyzed chemoselective reduction of alpha,beta-unsaturated aldehydes using CO and H₂O as the hydrogen source. *Chem. Commun.* **2010**, *46* (9), 1553–1555.
- (110) Li, S. S.; Liu, X.; Liu, Y. M.; He, H. Y.; Fan, K. N.; Cao, Y. Efficient and exceptionally selective semireduction of alkynes using a supported gold catalyst under a CO atmosphere. *Chem. Commun.* **2014**, *50* (42), 5626–5628.
- (111) Liu, L.; Qiao, B.; Chen, Z.; Zhang, J.; Deng, Y. Novel chemoselective hydrogenation of aromatic nitro compounds over ferric hydroxide supported nanocluster gold in the presence of CO and H₂O. *Chem. Commun.* **2009**, *6*, 653–655.
- (112) Mikami, Y.; Noujima, A.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Highly chemoselective reduction of nitroaromatic compounds using a hydroxalite-supported silver-nanoparticle catalyst under a CO atmosphere. *Chem. Lett.* **2010**, *39* (3), 223–225.
- (113) Dong, J.; Zhu, M.; Zhang, G.; Liu, Y.; Cao, Y.; Liu, S.; Wang, Y. Highly selective supported gold catalyst for CO-driven reduction of furfural in aqueous media. *Chin. J. Catal.* **2016**, *37* (10), 1669–1675.
- (114) Li, S.; Wang, F.; Liu, Y.; Cao, Y. Highly chemoselective reduction of nitroarenes using a titania-supported platinum-nanoparticle catalyst under a CO atmosphere. *Chin. J. Chem.* **2017**, *35* (5), 591–595.
- (115) Huang, J.; Yu, L.; He, L.; Liu, Y.-M.; Cao, Y.; Fan, K.-N. Direct one-pot reductive imination of nitroarenes using aldehydes and carbon monoxide by titania supported gold nanoparticles at room temperature. *Green Chem.* **2011**, *13* (10), 2672–2677.
- (116) Fujitani, T.; Nakamura, I.; Takahashi, A. H₂O dissociation at the perimeter interface between gold nanoparticles and TiO₂ is crucial for oxidation of CO. *ACS Catal.* **2020**, *10* (4), 2517–2521.
- (117) Daté, M.; Okumura, M.; Tsubota, S.; Haruta, M. Vital role of moisture in the catalytic activity of supported gold nanoparticles. *Angew. Chem.* **2004**, *116* (16), 2181–2184.
- (118) Zhao, S.; Chen, F.; Duan, S.; Shao, B.; Li, T.; Tang, H.; Lin, Q.; Zhang, J.; Li, L.; Huang, J.; Bion, N.; Liu, W.; Sun, H.; Wang, A. Q.;

Haruta, M.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Remarkable active-site dependent H₂O promoting effect in CO oxidation. *Nat. Commun.* **2019**, *10* (1), 3824.

(119) Saavedra, J.; Whittaker, T.; Chen, Z.; Pursell, C. J.; Rioux, R. M.; Chandler, B. D. Controlling activity and selectivity using water in the Au-catalysed preferential oxidation of CO in H₂. *Nat. Chem.* **2016**, *8* (6), 584–589.

(120) Wang, T.; Xing, J.-Y.; Jia, A.-P.; Tang, C.; Wang, Y.-J.; Luo, M.-F.; Lu, J.-Q. CO oxidation over Pt/Cr_{1.3}Fe_{0.7}O₃ catalysts: Enhanced activity on single Pt atom by H₂O promotion. *J. Catal.* **2020**, *382*, 192–203.

(121) Wang, C.; Gu, X.-K.; Yan, H.; Lin, Y.; Li, J.; Liu, D.; Li, W.-X.; Lu, J. Water-mediated Mars–Van Krevelen mechanism for CO oxidation on ceria-supported single-atom Pt₁ catalyst. *ACS Catal.* **2017**, *7* (1), 887–891.

(122) Shang, C.; Liu, Z. P. Origin and activity of gold nanoparticles as aerobic oxidation catalysts in aqueous solution. *J. Am. Chem. Soc.* **2011**, *133* (25), 9938–9947.

(123) Ide, M. S.; Davis, R. J. The important role of hydroxyl on oxidation catalysis by gold nanoparticles. *Acc. Chem. Res.* **2014**, *47* (3), 825–833.

(124) Yao, S.; Zhang, X.; Zhou, W.; Gao, R.; Xu, W.; Ye, Y.; Lin, L.; Wen, X.; Liu, P.; Chen, B.; Crumlin, E.; Guo, J.; Zuo, Z.; Li, W.; Xie, J.; Lu, L.; Kiely, C. J.; Gu, L.; Shi, C.; Rodriguez, J. A.; Ma, D. Atomic-layered Au clusters on alpha-MoC as catalysts for the low-temperature water-gas shift reaction. *Science* **2017**, *357* (6349), 389–393.

(125) Ge, Y.; Qin, X.; Li, A.; Deng, Y.; Lin, L.; Zhang, M.; Yu, Q.; Li, S.; Peng, M.; Xu, Y.; Zhao, X.; Xu, M.; Zhou, W.; Yao, S.; Ma, D. Maximizing the synergistic effect of CoNi catalyst on alpha-MoC for robust hydrogen production. *J. Am. Chem. Soc.* **2021**, *143* (2), 628–633.

(126) Deng, Y.; Ge, Y.; Xu, M.; Yu, Q.; Xiao, D.; Yao, S.; Ma, D. Molybdenum Carbide: Controlling the Geometric and Electronic Structure of Noble Metals for the Activation of O-H and C-H Bonds. *Acc. Chem. Res.* **2019**, *52* (12), 3372–3383.

(127) Deng, Y.; Gao, R.; Lin, L.; Liu, T.; Wen, X. D.; Wang, S.; Ma, D. Solvent tunes the selectivity of hydrogenation reaction over alpha-MoC catalyst. *J. Am. Chem. Soc.* **2018**, *140* (43), 14481–14489.

(128) Li, S.; Cao, R.; Xu, M.; Deng, Y.; Lin, L.; Yao, S.; Liang, X.; Peng, M.; Gao, Z.; Ge, Y.; Liu, J.-X.; Li, W.-X.; Zhou, W.; Ma, D. Atomically dispersed Ir/alpha-MoC catalyst with high metal loading and thermal stability for water-promoted hydrogenation reaction. *Natl. Sci. Rev.* **2021**, *1*.

(129) Khan, S. H.; Matei, G.; Patil, S.; Hoffmann, P. M. Dynamic solidification in nanoconfined water films. *Phys. Rev. Lett.* **2010**, *105* (10), 106101.

(130) Griffith, E. C.; Vaida, V. In situ observation of peptide bond formation at the water-air interface. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (39), 15697–15701.

(131) Zhang, M.; Wang, M.; Xu, B.; Ma, D. How to measure the reaction performance of heterogeneous catalytic reactions reliably. *Joule* **2019**, *3* (12), 2876–2883.

(132) Sievers, C.; Noda, Y.; Qi, L.; Albuquerque, E. M.; Rioux, R. M.; Scott, S. L. Phenomena affecting catalytic reactions at solid-liquid interfaces. *ACS Catal.* **2016**, *6* (12), 8286–8307.

(133) Bjorneholm, O.; Hansen, M. H.; Hodgson, A.; Liu, L. M.; Limmer, D. T.; Michaelides, A.; Pedevilla, P.; Rossmeisl, J.; Shen, H.; Tocci, G.; Tyrode, E.; Walz, M. M.; Werner, J.; Bluhm, H. Water at Interfaces. *Chem. Rev.* **2016**, *116* (13), 7698–7726.

(134) Xiong, H.; Pham, H. N.; Datye, A. K. Hydrothermally stable heterogeneous catalysts for conversion of biorenewables. *Green Chem.* **2014**, *16* (11), 4627–4643.

(135) Pham, H. N.; Anderson, A. E.; Johnson, R. L.; Schmidt-Rohr, K.; Datye, A. K. Improved hydrothermal stability of mesoporous oxides for reactions in the aqueous phase. *Angew. Chem.* **2012**, *124* (52), 13340–13344.

(136) Yu, L.; Deng, D.; Bao, X. Chain mail for catalysts. *Angew. Chem., Int. Ed.* **2020**, *59* (36), 15294–15297.