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Water-assisted oxygen activation during selective oxidation reactions

Hung-Vu Tran¹, Hieu A Doan¹, Bert D Chandler² and Lars C Grabow¹

The selective functionalization of hydrocarbons with oxygen to produce valuable commodity chemicals is inherently challenging, because of the thermodynamic stability of the complete combustion products. Emerging green synthesis routes and sustainable energy production also rely on the success of selective oxidation reactions. As one of the unselective by-products, water is always present under reaction conditions and numerous studies indicate that the catalytic activity and selectivity of selective oxidation reactions may be tuned by judiciously controlling the water content during the reaction. Some experimentally verified examples include the preferential oxidation of carbon monoxide, direct hydrogen peroxide synthesis, propene epoxidation and alcohol oxidation. Finally, it has been predicted that the direct conversion of methane to methanol can benefit from the right amount of water near the active site during oxygen activation.

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Introduction

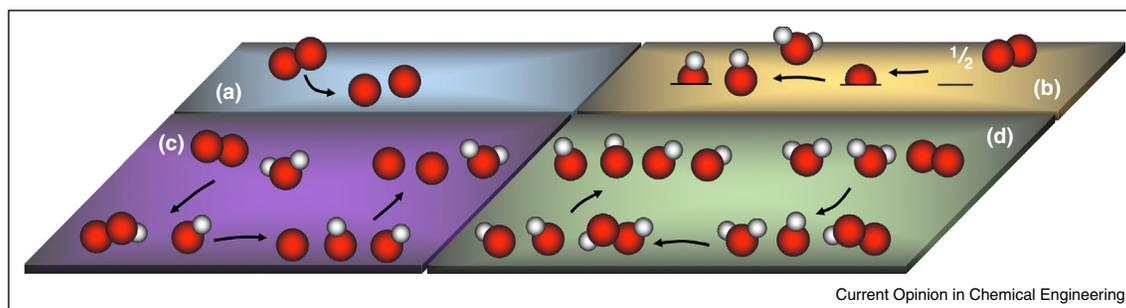
Numerous recent studies have eluded to the phenomenon that the presence of water (H₂O) in quantities ranging from a few ppm to aqueous solutions can significantly increase reaction rates and, more importantly, the selectivity for certain partial oxidation reactions. This effect is observed in both homogeneously [1,2] and heterogeneously [3*,4*,5*] catalyzed reactions. While water may affect catalytic reactions in multiple ways, its ability to shuttle protons to and from reactants, intermediates and products can directly change the course of a reaction. In aqueous,

homogeneous environments the facile proton transfer is known as the Grotthuss mechanism and is rather well understood [6,7]. In contrast, the co-catalytic effect of water in heterogeneously catalyzed reactions has only recently started to attract attention. In 2012, for example, Merte *et al.* used a combination of high-speed, high-resolution scanning tunneling microscopy, isotope-exchange experiments and density functional theory (DFT) calculations to identify a novel water-mediated proton diffusion mechanism on a FeO/Pt(111) surface at low temperatures [8*]. The participation of a water molecule during proton hopping allows the formation of an H₃O⁺-like transition state, which lowers the activation energy barrier from 1.02 eV to only 0.21 eV, equivalent to a 16-fold increase in the diffusion rate at room temperature. A more recent *ab initio* molecular dynamics study provides evidence for a Grotthuss-like, water-mediated mechanism for fast and long-range proton diffusion at the Pt/CeO₂ interface [9*].

Partial oxidation reactions are universally challenged by the relative thermodynamic instability of the desired products compared to the total oxidation products (water and carbon dioxide, CO₂) [10]. Further, partial oxidations are typically exothermic, providing the necessary energy for deeper oxidation reactions. Thus, successful examples of difficult direct selective oxidations are rare. Notable progress has been made using non-traditional oxidants and/or noble metal catalysts at low to moderate temperatures. In particular, soft oxidants, e.g. sulfur [11,12], or noble metals such as gold, silver, or copper in combination with hydrogen peroxide (H₂O₂) or nitrous oxide (N₂O) seem promising [10]. The strong oxidizing power of H₂O₂ along with its environmentally friendly product (water) make it a noteworthy alternative oxidant. It also reacts more readily on noble metals, which are less suited to catalyze the direct dissociation of molecular oxygen (O₂) shown in Scheme 1(a). H₂O₂ is currently produced in the multistep anthraquinone process, which requires the use of mixtures of organic solvents and liquid extraction steps. Thus, the production and abatement of harmful by-products increases synthesis costs and results in a negative environmental impact [13]. Attempts are underway to develop green H₂O₂ synthesis routes directly from O₂ and H₂ [14,15**], but safety concerns from handling and transporting H₂O₂, or potentially explosive mixtures of H₂ and O₂, remain.

The reaction intermediates derived from H₂O₂ as an oxidant are generally considered to be surface bound

Scheme 1



Formation of active oxygen intermediates from O₂: (a) O₂ dissociation; (b) hydroxyl formation with a pre-existing O atom (in the common case of metal-oxides, the pre-existing O atom is a lattice oxygen); (c) water-assisted O₂ dissociation; and (d) O₂ activation with excess water.

hydroperoxyl (OOH) and hydroxyl (OH), both of which can also be produced from H₂O and O₂ via the proton exchange sequences illustrated in Scheme 1(c),(d). Water and oxygen are environmentally benign, suggesting that sustainable synthesis routes for challenging selective oxidation reactions exist. In this context, we provide a concise review of notable accomplishments since 2012 on heterogeneously catalyzed selective oxidation reactions that use water as a co-catalyst to activate oxygen via proton transfer steps. In the interest of brevity we limit this review to (preferential) carbon monoxide (CO) oxidation, propylene epoxidation, alcohol oxidation, and methane partial oxidation; we note many other examples also exist [16^{**},17^{**},18,19^{**},20^{*},21^{*},22^{**},23^{**},24,25^{**}]. For the role of water in homogeneously catalyzed reactions and solvent effects on transition state stability we refer interested readers to previous reviews [1,5^{*},26].

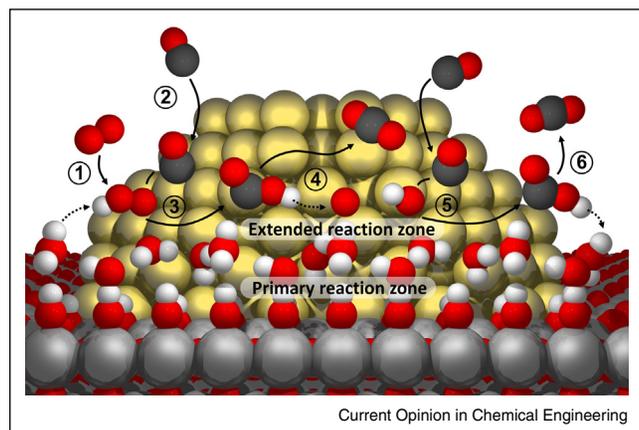
Selective oxidations involving carbon monoxide (CO) and hydrogen (H₂)

With applications in vehicle-exhaust emission control, and H₂ production/purification for proton-exchange-membrane (PEM) fuel cells and ammonia synthesis, transition metal catalyzed CO oxidation ($\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$) is of substantial interest [27–30]. CO oxidation is routinely used as the prototypical model reaction in heterogeneous catalysis research because it is seemingly simple, yet exhibits a variety of complex phenomena [27,28,31]. Highlights include Ertl's observation of temporal oscillations and spatial pattern formation on Pt(110) [27], Goodman's work on bridging the pressure gap on Pt-group metals [32], and Haruta's breakthrough discovery that nanoparticulate gold is highly active for CO oxidation even below room temperature [33,34]. This discovery undoubtedly marks the beginning of the 'gold rush' in heterogeneous catalysis leading to an astonishing > 5,000 papers published since 1987 and summarized in several review articles [34–39]. The bulk of the early studies concerns the dependence of catalytic activity on the Au nanoparticle size, the effect of various metal oxide support types, and more generally the

nature of the active site, while the presence of moisture and its benefits for CO oxidation activity has been the topic of more recent studies [3^{*},4^{*},34]. The effect of moisture is in fact remarkable; co-feeding small amounts of water (as little as 200 ppm) leads to a larger than 10-fold increase in CO oxidation activity of Au/SiO₂ at 0 °C [40]. Proposed roles of water during CO oxidation on Au can be categorized as: (i) creation of cationic gold atoms as active sites; (ii) transformation and decomposition of stable carbonate intermediates blocking reaction sites; (iii) direct participation in CO₂ formation; and (iv) activation of oxygen [4^{*}]. Roles (i)-(iii) are specific to CO oxidation on Au, but phenomenon (iv), oxygen activation, is common to aerobic oxidations over numerous types of catalysts. We therefore concentrate on the role of water in oxygen activation during CO oxidation, and note that other factors specific to each reaction system also exist. We also highlight that water's direct participation as a co-catalyst in CO₂ formation is distinct from the water-gas shift (WGS) reaction. In WGS catalysis, water is a reactant, regenerating surface hydroxyl groups, which react with CO.

Strict differentiation between the effect of water and the catalyst support is elusive. Unless studied under well-controlled, ultra high vacuum (UHV) conditions, metal-oxides generally form surface hydroxyl groups (s-OH) according to Scheme 1(b). These support hydroxyls may react directly with CO to form the carboxyl (COOH) intermediate [39]. Daniells *et al.* used a high temperature pre-treatment for Au/Fe₂O₃ catalysts to remove support hydroxyls as water, finding that CO oxidation activity was drastically reduced for the dehydroxylated material [41]. Surface dehydration was confirmed by water detection during temperature programmed desorption (TPD). Consequently, Bond and Thompson proposed that water promotes CO oxidation by maintaining the concentration of reactive s-OH groups from the reaction of water with the metal oxide support [39]. Lattice oxygen atoms removed as CO₂ are ultimately replaced by O₂ in a

Figure 1



Proposed mechanism for water-assisted CO oxidation over Au/TiO₂. The reaction steps are (1) s-H₂O + O₂ + Au → Au-OOH + s-OH; (2) CO + Au → Au-CO; (3) Au-CO + Au-OOH → Au-COOH + Au-O; (4) Au-COOH + Au-O → CO₂ + Au-OH + Au; (5) Au-CO + Au-OH → Au-COOH + Au; and (6) Au-COOH + s-OH → CO₂ + Au + s-H₂O. From reference [16]. Reprinted with permission from AAAS.

Mars-van-Krevelen type mechanism. Although the direct involvement of s-OH and lattice oxygen atoms has been frequently suggested, carefully conducted isotope labeling experiments demonstrate that lattice oxygen is not a reactive oxygen source and that observed oxygen exchange is due to secondary scrambling effects [22^{••},42].

Water-assisted activation of O₂ to form a reactive OOH intermediate, shown in Scheme 1(c), has also been invoked to explain gold's oxidation activity [22^{••},43]. In fact, many conflicting interpretations can be reconciled by the CO oxidation mechanism illustrated for Au/TiO₂ in Figure 1 [16^{••}]. Using *in situ* infrared spectroscopy to quantify the amount of s-OH groups and molecularly adsorbed water, a strong correlation between weakly bound surface water and the reaction rate was found. Furthermore, a H/D kinetic isotope effect (KIE) of nearly 2 was measured, indicating that a proton transfer step is involved in the rate-determining step of the reaction. Complimentary DFT calculations suggested that s-OH groups at the Au/TiO₂ interface are necessary to anchor water molecules near Au via hydrogen bonding. These water molecules can then serve as proton source to form the reactive Au-OOH species in a barrier free proton transfer step to adsorbing O₂. The Au-OOH intermediate subsequently reacts with Au-CO to generate an Au-COOH intermediate. Notably, the O-OH bond cleavage in the presence of Au-CO requires an activation barrier of only 0.1 eV, thereby constituting one of the lowest reported energy pathways for O₂ activation. The KIE was attributed to the rate-determining second proton transfer from Au-COOH back to the adsorbed water layer,

which is necessary to release CO₂ and close the catalytic cycle. The barrier for this step decreases further when additional water molecules are present, consistent with the experimentally observed equilibrium isotope effect under very wet conditions [22^{••}].

Based on the newly established water-assisted mechanism [16^{••}], record-breaking improvements to the preferential oxidation (PROX) of CO with O₂ in an H₂-rich environment have been reported [17^{••}]. Rather than designing a new catalyst, a commercial Au/Al₂O₃ catalyst and optimized feed water content achieved unprecedented CO conversion and O₂-to-CO₂ selectivity. Under optimal conditions, CO slip could be reduced to below 10 ppm, while maintaining 80-90% O₂-to-CO₂ selectivity. The surface water concentration on the Al₂O₃ support under these conditions was quantified to be ca. 1-2 monolayers, and is nearly identical to the optimal support water coverage for CO oxidation on Au/TiO₂ [16^{••}]. The high selectivity for CO oxidation over H₂ oxidation was in part attributed to the increased CO oxidation rate, but also to the blockage of H₂ dissociation sites near the Au/Al₂O₃ interface by water. This is an exceptional example of how fundamental mechanistic insight can pave the road for major scientific advances with direct relevance to industrially important processes.

Similar water-assisted CO oxidation mechanisms have not only been proposed for Au, but also for Ag [18], and Pt [22^{••},44] catalysts. Sheu and Chang used DFT to study CO oxidation on the water pre-covered Ag(111) surface, proposing the formation of OOH according to Scheme 1(c) [18]. The remainder of the proposed mechanism shares many steps with the mechanism depicted in Figure 1. This includes the rate-determining decomposition of COOH by proton transfer to OH to form CO₂ and to regenerate the H₂O co-catalyst. The two mechanisms differ in the reaction step between OOH and CO forming either COOH + O [16^{••}] or CO₂ + OH [18] as products.

The promotional effect of water on O₂ activation is not limited to noble metals, on which O₂ activation is inherently difficult. An exhaustive mechanistic study by Iglesia and co-workers showed that O₂ pre-activation to OOH via a proton transfer from H₂O on Pt/Al₂O₃ catalyst also accelerates the rate of CO oxidation [22^{••}]. Changing from dry to wet conditions (0 kPa to 0.5 kPa of H₂O) causes the rate per surface atom to increase from 0.08 to 0.28 mol s⁻¹ g-at Pt_s⁻¹. For comparison, the equivalent rate increase over Au/Al₂O₃ (0.08 to 2.55 mol s⁻¹ g-at Au_s⁻¹) is much larger. Although CO oxidation over Pt and Au is limited by the ability to activate O₂, the difference in sensitivity to the water coverage speaks to the existence of different reasons for difficult O₂ activation. Unlike Au, Pt is capable of dissociating O₂, but its strong affinity for CO leads to high CO coverage and surface poisoning. While the presence of H₂O may lower the

CO surface coverage, it can also decrease the barrier for O₂ dissociation on the remaining vacant sites, and in turn lead to higher CO oxidation rates. Indeed, the lower barrier pathway for O₂ activation via the OOH intermediate is reflected in an 18 kJ/mol lower apparent activation energy in the presence of H₂O. In contrast, Au is not inhibited by high CO coverage and water is involved in both O₂ binding and COOH decomposition; thus, the promotional effect of water on O₂ activation is more pronounced.

In contrast to the discussion thus far, complete O-O bond activation is undesired when it comes to direct H₂O₂ synthesis. Nevertheless, Wilson and Flaherty have demonstrated that high proton concentrations result in improved selectivity and turnover frequency for H₂O₂ production over Pd/SiO₂ catalysts in protic solvents (water and methanol) [15^{**}]. A thorough kinetic analysis explained this in terms of a competition between OOH dissociation and further protonation to yield H₂O₂. This difference is also captured in Scheme 1(d), in which the abundance of protons (here shown to originate from H₂O) favors the rapid formation of H₂O₂ prior to the formation of OH. As Wilson and Flaherty alluded, secondary O-O bond scission in H₂O₂ may be reduced when larger Pd particles with a higher fraction of coordinated Pd atoms are used.

Propylene epoxidation

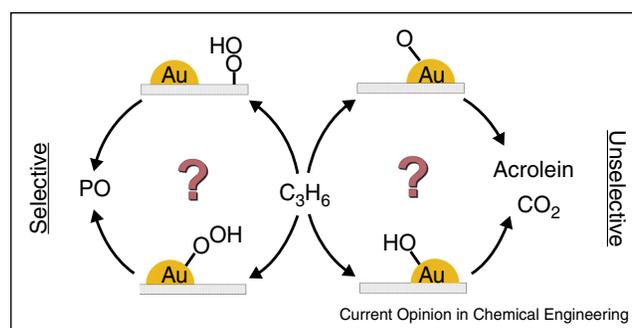
Propylene oxide (PO) is one of the most important commodity chemicals with more than 7 million tons annual worldwide market capacity [34]. Polyurethane, polyether polyols, glycol ethers, and propylene glycols are just a few of the various compounds produced from PO [45]. The ideal process for PO production, which is analogous to ethylene epoxidation over silver catalysts, is the selective epoxidation of propylene with molecular O₂: C₃H₆ + ½O₂ → C₃H₆O [46,47]. This goal, however, has not yet been achieved and is considered by some as a Holy Grail in catalysis [34]. Current industrial PO production requires the use of chlorohydrin, organic hydroperoxides, or hydrogen peroxide in the so-called hydrogen peroxide to propylene oxide (HPPO) process [48]. While each process has its own advantages, they either require toxic, corrosive, expensive to transport reagents, or produce harmful by-products, whose separation, abatement or recycling adds to the overall process cost [34]. Progress toward safer and sustainable PO production may be achieved by eliminating hydrogen peroxide in the HPPO process through *in situ* generation of the right oxygen-containing intermediates. With Au/TiO₂ being a known selective catalyst for direct H₂O₂ synthesis from a mixture of O₂/H₂, Haruta *et al.* confirmed the feasibility of *in situ* H₂O₂ generation on gold nanoparticles deposited on Ti-containing supports for the selective epoxidation of propylene [34,45,49]. Although these results are promising, the primary remaining barriers

are poor hydrogen efficiency due to hydrogen oxidation to water, and the potential explosion risk when working with H₂/O₂ mixtures.

Active oxidants derived from H₂O₂ are likely surface-bound OOH and OH, which can also be generated from a mixture of O₂ and H₂O (Scheme 1(c),(d)). Thus, it is reasonable to expect that controlled amounts of added water can assist during O₂ activation, forming the oxygen-containing surface intermediates required for selective propylene epoxidation. Consequently, the research groups of Iglesia, Haruta, and Vajda have independently pursued this idea on various supported gold catalysts [50–52]. Ojeda and Iglesia [50] used TiO₂ supported Au nanoclusters (~3.3 nm) and reported up to 70% PO selectivity. Haruta and co-workers found that 50% PO selectivity could be achieved over 1.0–2.0 nm small Au clusters supported on alkaline-treated titanasilicalite-1 (TS-1) [51,53]. Even smaller particles, i.e. Au₆₋₁₀ clusters with diameters below 1.0 nm, supported on three monolayer thin films of Al₂O₃ grown by atomic layer deposition (ALD) were used by Vajda and co-workers, resulting in up to 90% PO selectivity [52]. The selectivity to PO in all three studies drops drastically when water was removed from the feed; in the absence of water, PO production was no longer observed. It is evident from these experiments that water plays a vital role in promoting the desired epoxidation reaction.

Figure 2 provides a generic reaction scheme for supported Au propylene epoxidation catalysts. Selective PO production is attributed to the reaction of propylene with either Au-OOH or s-OOH, both of which are formed by water-assisted (proton transfer) O₂ activation (Scheme 1(c)). In the case of TS-1 as support a correlation between the variation in the UV/Vis band characteristic for Ti-OOH and the production of PO is consistent with Ti-OOH as the active oxygen intermediate [51]. The same conclusion was reached in a kinetic study by Perez Fernandez *et al.* [25^{**}]. Both groups agree that Au-O species are

Figure 2



The roles of various oxygen containing reaction intermediates derived from O₂/H₂O in the selective epoxidation of propylene.

responsible for the formation of the undesired products CO_2 and acrolein.

Theoretical studies are largely congruent with the water-assisted mechanism shown in Figure 2. Yet, the computational results also indicate that the reaction is structure sensitive, and that water participates indirectly by changing the nanoparticle structure and stabilizes transition states by solvation effects [19^{••},52,54]. For unsupported Au cluster models of 10 and 38 atoms, Li and co-workers calculated a barrier for proton transfer from water to co-adsorbed O_2 of only ~ 0.2 eV [54]. The subsequent reaction between Au-OOH and propylene to form PO requires a barrier of ca. 0.8 eV for Au_{10} and 1.0 eV for Au_{38} . The same group used a combination of global minimum searches and *ab initio* molecular dynamics and determined that initially upright Au_7 clusters on fully hydroxylated $\alpha\text{-Al}_2\text{O}_3(0001)$ transform into flat geometries when hydroxyl groups are removed as water [19^{••}]. This structural reconstruction, however, does not affect the finding that Au-OOH is the selective intermediate leading to epoxidation. The barrier for Au-OOH formation via proton transfer from s- H_2O to Au- O_2 is sensitive to the amount of water present and is lowered from 0.34 eV to 0.16 eV, when an additional s- H_2O molecule is included in the simulation. The disparate conclusion regarding the selective epoxidation species, Au-OOH for Au/ Al_2O_3 vs. s-OOH for Au/TS-1, may be explained by the different support materials used.

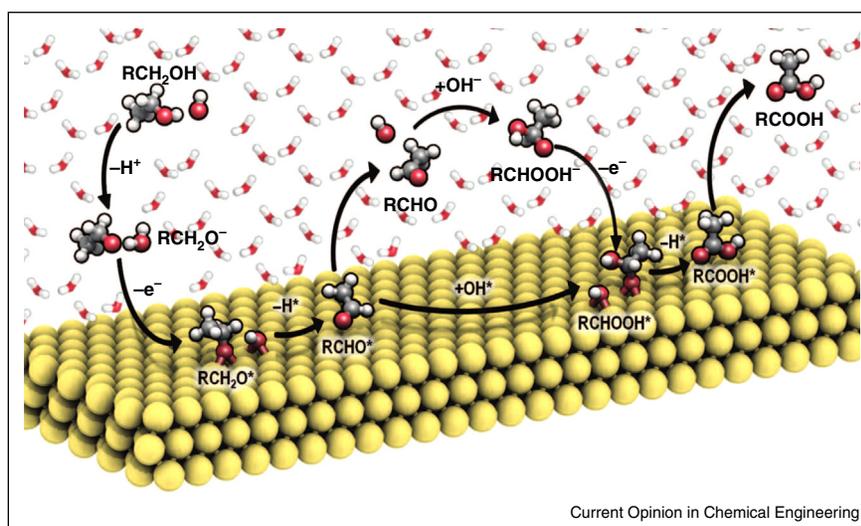
Although a general consensus exists for OOH (either in the form of s-OOH or Au-OOH) leading to the desired epoxidation of propylene, the pathways leading to the non-selective side products CO_2 and acrolein are still debated. Some attribute the formation of undesired products to the

existence of Au-OH [19^{••}], while others have suggested Au-O as the responsible surface species [25^{••},51]. More research efforts will be necessary to fully elucidate the specific roles of Au-O and Au-OH and to enable the design of catalysts with improved PO selectivity.

Alcohol oxidation

The liquid phase aerobic, selective oxidation of alcohols to value-added products (e.g. aldehydes, ketones or carboxylic acids) over solid catalysts is an industrially desired process and was reviewed by Mallat and Baiker in 2004 [55]. Since then numerous studies have appeared discussing the mechanistic implications of water on the product selectivity using Au-based catalysts [56–60]. The theme of this review, combining selective noble metal catalysts with O_2 activation by water-mediated proton transfer chemistry, was successfully followed by Davis and co-workers, who developed methods for the aqueous aerobic oxidation of glycerol to glyceric acid and other partial oxidation products over Au and Au-Pd alloy catalysts [61,62]. Additional insight into the reaction mechanism was obtained from kinetic $^{18}\text{O}_2$ and H_2^{18}O labeling experiments over Au/C, Au/ TiO_2 , Pd/C, and Pt/C catalysts combined with DFT calculations in collaboration with Neurock's group [20[•]]. Under high pH conditions ($\text{pH} > 13$) the Au-based catalysts exhibited higher turnover frequencies (TOF) than the Pd and Pt catalysts tested under identical conditions. In the absence of added base, Au was inactive. Adsorbed Au-OH and hydroxide ions (OH^-) in solution were ultimately identified as active species (Figure 3). Isotope labeling and DFT models supported the authors conclusion that O_2 is needed to regenerate Au-OH/ OH^- through the *in situ* formation of hydrogen peroxide and its subsequent decomposition to 2 Au-OH groups. As the O_2 activation

Figure 3



Reaction scheme for the oxidation of alcohols to acids over a Au surface in water at high pH. Hydroxide facilitates elementary steps in alcohol oxidation in both the solution phase and at the metal/solution interface. From reference [20[•]]. Reprinted with permission from AAAS.

pathway in Scheme 1(d) shows, it requires more water and an additional proton transfer step than the mechanism depicted in Scheme 1(c). Considering the water-rich environment in aqueous solution and the low calculated proton transfer barriers, the mechanism in Scheme 1(d) is entirely plausible.

A variation of this mechanism has been proposed by Chang and co-workers based on their DFT work on methanol oxidation to formaldehyde on Au(111) surfaces [63]. The calculated barriers for Au-O, Au-OH and Au-OOH-mediated methanol oxidation steps are all reasonably low, such that any of these surface intermediates are feasible oxidants. The endothermic formation of Au-OOH via the steps shown in Scheme 1(c), however, was suggested as rate-determining step. This conclusion was drawn based on a calculated activation barrier of 0.91 eV for the proton transfer from H₂O to O₂. In the presence of a second water molecule this barrier drops to 0.45 eV, and Au-OOH dissociation to Au-OH and Au-O turns into the highest activated step with a barrier of 0.79 eV. The fact that Chang's group concluded that water-assisted O₂ activation is rate limiting is likely a consequence of choosing bulk-like Au(111) as model surface. Thus, this finding is not necessarily in conflict with other studies; it rather manifests that Au-catalysis is strongly dependent on electronic and geometric factors, i.e. particle size, and support effects.

Methane-to-methanol

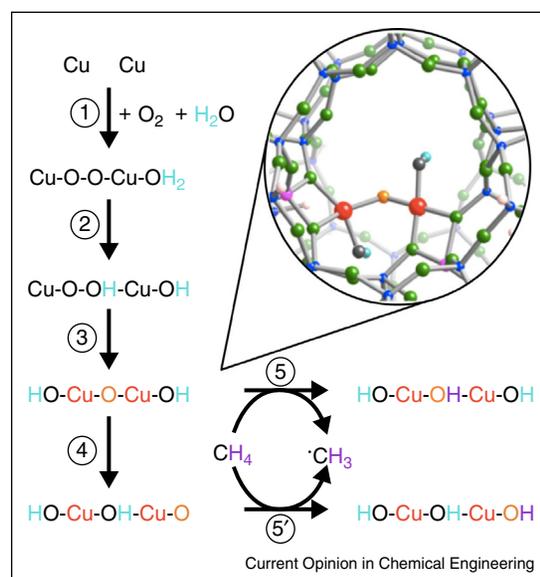
Despite decades of research, the selective partial oxidation of methane-to-methanol remains one of the last frontiers in modern chemistry [64,65]. Inspired by nature's monooxygenase (MMO) enzyme, whose active site is composed of an Fe center in its soluble form (sMMO) and a Cu center in its particulate form (pMMO) [10], Hutchings' group studied Cu-promoted Fe/ZSM-5 and achieved three orders of magnitude higher methane-to-methanol activity than previously reported [21*]. The caveat to this discovery is the need for hydrogen peroxide as oxidant. Nevertheless, research on Fe and Cu exchanged zeolites, primarily with MFI or MOR framework structure, has rapidly intensified in recent years [64–67]. Owing to its superior activity and selectivity, Cu/ZSM-5 with MFI structure has attracted great interest; its active site was identified as a mono(μ -oxo) dicopper core, [Cu-O-Cu]²⁺ [68]. Compared to the 10-membered ring channels in MFI, the MOR structure has larger 12-membered ring pores that stabilize a trinuclear copper-oxo cluster [69]. The active site containing extra-framework radical oxygen is generated from the Cu-exchanged zeolite by an appropriate oxygen treatment followed by exposure to methane to form methanol.

Water is regularly employed in methane-to-methanol studies on Cu-exchanged zeolites, but with the purpose to purge the zeolite framework and extract the strongly

adsorbed methanol product. Indeed, DFT studies for Cu/MOR confirm that competitive water adsorption facilitates the release of methanol [70]. Yet, to date, no direct experimental evidence for water-assisted oxygen activation pathways during partial oxidation of methane on metal-exchanged zeolites has been reported. According to the DFT study by Yumura and co-workers, however, the presence of a single H₂O molecule near the dicopper site in ZSM-5 enhances the activation of dioxygen via proton transfer analogous to Scheme 1(c), whereas a second H₂O molecule inhibits the reaction [23**]. Given the ubiquitous presence of trace amounts of water in even ultra high purity gases, it is entirely plausible that this pathway contributes to the observed activity.

The proposed water-mediated mechanism for methane activation over Cu/ZSM-5 is illustrated in Figure 4 [23**]. Adsorption of O₂ and H₂O to the dicopper site (step 1) forms the *trans*- μ -1,2-peroxo dicopper complex (Cu-O-O-Cu-OH₂). Next, one proton is transferred from adsorbed H₂O to O₂, generating the Cu-O-OH-Cu-OH intermediate (step 2, cf. Scheme 1(c)). The hydroperoxo O-OH bond then breaks (step 3), forming the radical oxygen containing species HO-Cu-O-Cu-OH shown in the inset of Figure 4. An alternative radical oxygen containing isomer HO-Cu-OH-Cu-O can also be generated along step 4. Both of these radical oxygen complexes are capable of abstracting a H• atom from methane, forming CH₃• (steps 5 and 5'). Similar radical oxygen containing complexes can be formed by the water-promoted O₂ activation on Cu/ZSM-5 possessing a trinuclear copper core, indicating that the water-assisted mechanism may also apply to Cu/MOR and possibly

Figure 4



Predicted methane activation pathways over Cu/ZSM-5 catalyst assisted by water. Adapted from Reference [23**].

other Cu-exchanged zeolites [23^{••},69]. Further, these oxo-mediated radical abstraction processes are essentially the same types of mechanisms employed by MMO enzymes [10], which suggests that this may be a very general C-H activation pathway. Verification of this theoretical prediction requires precise control of the water content inside the zeolite pore and may prove difficult, but the potential impact of a successful demonstration should provide sufficient motivation.

Summary and Outlook

In general, the use of noble metal catalysts, especially Au, and mild to moderate reaction conditions favors partial oxidation products. In these catalytic systems, O₂ delivery can be controlled and selectivity is improved by avoiding overoxidation and complete combustion. The selectivity improvement often comes at the cost of low conversion causing overall process yields to remain below industry targets. A possible solution is a transition to more readily activated oxidizing agents, but these reactants are often costly, may have adverse environmental effects, and are typically more difficult to handle than O₂.

Water-assisted O₂ activation in mixtures of O₂ and H₂O is a new and promising approach to challenging partial oxidations. While the sequence of elementary steps varies for different catalysts and reaction conditions, there is general agreement that facile proton transfer steps between H₂O and O₂ lead to the formation of surface bound OOH, OH, and/or O species. These are the same surface intermediates as those derived from H₂O₂, implying that expensive H₂O₂ may ultimately be replaced by mixtures of H₂O and O₂ with minimal modifications to the catalyst. Moreover, the concentration and type of active oxygen species on the catalyst surface may be optimized through precise control of the amount of water (or protons) present during the reaction. Despite the reported benefits of water as a co-catalyst, care must be taken to avoid excess water conditions for systems in which H₂O competitively adsorbs on reaction sites and thereby limits the adsorption of other reactants. An example of strong water inhibition is the oxidation of small alkanes on PdO, where surface hydroxylation has been associated with catalyst deactivation [71].

We emphasize that water-assisted O₂ activation is not only relevant to gold, on which O₂ dissociation in the absence of water is difficult, but it also applies to Pt-group and other transition metal alloys for reactions in which O₂ dissociation is rate-determining. It is important to note that even when water is not deliberately added, it can hardly be avoided as a by-product during partial oxidation reactions. Thus, the water-mediated activation of O₂ should always be considered as a potential catalytic pathway.

As heterogeneous catalysis research moves forward to make significant advances and new scientific discoveries, we believe the following key questions related to the role

of proton mobility during O₂ activation should be addressed. For oxide supported metal catalysts, the local water structure and proton transfer at the three-phase boundary between the oxide, metal and fluid phase must be carefully characterized. Concomitantly, a predictive method for the amount and type of oxygen intermediates formed on the metal and the support as function of reaction conditions must be developed. This concept should then be expanded by considering a broader class of proton sources and shuttles, for example, alcohols or carboxylic acids. Finally, a better mechanistic understanding of which oxygen species participate in desired and undesired oxidation pathways is required to improve selectivity and atom-efficiency. Besides catalytic oxidation reactions, water-mediated proton transfer has other far-reaching implications, for instance, in catalytic hydrodeoxygenation of bio-oil [72], electrocatalysis [73–75], and any reaction using solid acid catalysts including zeolites [76,77]. Thus, we see numerous opportunities for innovative research on water-assisted catalysis in diverse areas that may ultimately lead to disruptive technologies.

Acknowledgements

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
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