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Solvation-induced changes of the mechanism of alcohol oxidation at aqueous *versus* gas phase Au/TiO₂ nanocatalysts

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Abstract: Gold/titania catalysts are widely used for key reactions, notably including the selective oxidation of alcohols in the liquid phase. Our large-scale *ab initio* simulations disclose that the liquid-phase reaction mechanism is distinctly different from that in the gas phase due to active participation of water molecules. While concerted charge transfers related to O₂ splitting and abstraction of both, protonic and hydridic hydrogens are enforced under dry conditions, step-wise charge transfer is preferred in the condensed phase. Dissociation of reactive water molecules and subsequent Grotthuss migration of protonic defects, H⁺(aq), allows for such a decoupling of the oxidation process, both in time and space. It is expected that these observations are paradigmatic for heterogeneous catalysis in aqueous phases.

In recent years, titania has become the subject of countless investigations because of its very interesting electronic properties and outstanding chemical reactivity, [1, 2] especially as a photocatalyst. [3] In addition, when used as support for gold nanoparticles (AuNP), the resulting Au/TiO₂ system shows remarkable performance as a catalyst for a myriad of reactions, [4, 5] not only as a photocatalyst but also upon thermal activation. [6] Specifically, Au/TiO₂ is widely used to catalyze oxidation reactions [7] of many species such as H₂, [8] CO [9, 10, 11, 12, 13] and alcohols [14, 15] to name but a few examples. For many such reactions on metal/oxide catalysts, great progress has been achieved toward understanding mechanisms in terms of the motion of individual atoms and the associated electronic structure changes in the spirit of the “Surface Science approach” to theoretical heterogeneous catalysis, [10, 12, 16] including

considering thermal and dynamical effects via *ab initio* molecular dynamics (AIMD) [17] simulations in some cases. [13, 18, 19]

In case of alcohol oxidation on Au/TiO₂, despite substantial experimental work on the gas phase reaction, [15, 20, 21, 22, 23, 24] the current theoretical understanding of this particular reaction in the liquid phase is *terra incognita* due to methodological obstacles, while other redox reactions in liquid-phase heterogeneous catalysis have been successfully investigated using AIMD. [25, 26, 27, 28] On the other hand, there exists already considerable experimental evidence of pronounced solvation effects on liquid-phase oxidation processes [16, 29, 30, 31, 32, 33, 34] in addition to recent reports on significant nanocatalyst/water cross talk at the level of AuNP dynamics and charge transfer. [35, 36] Obviously, water as a high-dielectric polar solvent can not only transfer charge and stabilize charged intermediates or transition states incomparably better than any gas phase can do, but as a protic solvent it can also be chemically engaged in reactions. Yet, despite its pivotal role in reaction mechanisms that govern liquid-phase heterogeneous catalysis the role of water as an active re-agent remains severely underresearched mainly due to technical challenges, both in experiment and theory.

In this Communication, we follow our “Solvation Science approach” to theoretical heterogeneous catalysis in the liquid phase. Thus, we take advantage of enhanced sampling AIMD [17] simulations using a well-established Au/TiO₂ nanocatalyst model [35, 37, 38, 39] in order to decipher the mechanistic details of thermally activated liquid-phase methanol oxidation at elevated *T* and *p* in accordance with experimental conditions [31] in one-to-one comparison to the gas phase process (see SI for methods, model and computational

details). Thus, all water molecules are explicitly included and consistently treated at the same electronic structure level as the catalytic species (Fig. 1). Moreover, AIMD in the absence of any water molecule allows us to probe oxidation in the presence of a gas phase at the same temperature. We will demonstrate that O_2 activation, which is known to preferentially occur at so-called perimeter sites of the AuNP/titania interface, [10, 12, 38] is enhanced in the liquid phase. Importantly, we disclose how the presence of reactive water molecules changes the liquid-phase reaction mechanism in distinct ways as compared to that in the gas phase, notably including Grotthuss-like charge transport contributions.

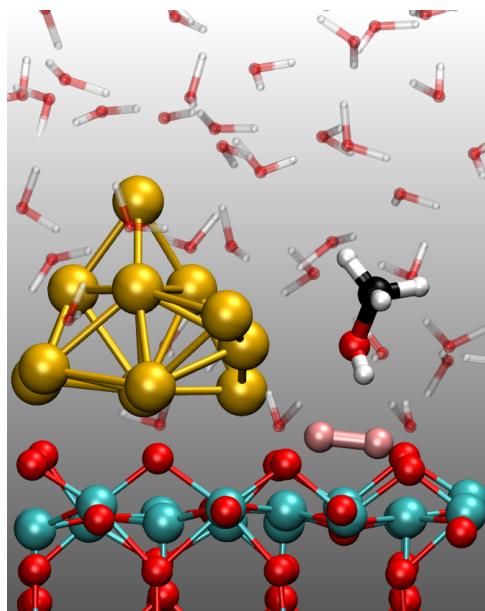


Figure 1: Close-up of the liquid-phase Au/TiO₂ nanocatalyst system used to simulate methanol oxidation in water by dioxygen that is activated at the AuNP/titania perimeter site. The TiO₂ slab is shown in red (O) and cyan (Ti), the AuNP in gold, the adsorbed O₂ in pink, the CH₃OH in black (C), red (O) and white (H), and the H₂O molecules in transparent red (O) and white (H).

Our results are based on three independent sets of multiple walkers *ab initio* metadynamics simulations [40] with the Au/TiO₂ nanocatalyst being in contact with the dioxygen and methanol reactants in the gas phase as well as in neutral and basic water (see SI for details). Let us set the stage by analyzing first the gas phase oxidation reaction as the reference process. Here, the methanol molecule is adsorbed *via* weak interactions of its OH group with pre-adsorbed O₂ (see structure a_G in Fig. 2). Several transient events are observed during the simu-

lation where one of the aliphatic hydrogens moves close enough to the AuNP (i.e. with an Au-H distance in the range of 1.6–1.9 Å), leading to C-H activation as evidenced by a concurrent elongation of the corresponding C-H bond from its equilibrium value of 1.1 Å to ~1.7 Å (see b_G in Fig. 2); we refer to the supporting Section II for comprehensive structural analyses.

These elongations are dynamically correlated with increasing Löwdin charges of the involved H atom and the AuNP in conjunction with simultaneously decreasing charges of the C atom and, to a lesser extent, also of the O atom in CH₃OH (Fig. 2, bottom-left and supporting Section II for the pertinent distances). Some of these events happen at the same time when the “acidic” hydroxyl hydrogen moved close enough to the O₂ molecule, which thus is shared as a proton in a “Zundel-like” arrangement (i.e. CH₃O⁻···H⁺···O₂, not shown in Fig. 2). However, as long as O₂ remains undissociated, neither the hydroxyl nor the aliphatic hydrogens are transferred to the AuNP or to the dioxygen species, respectively. Methanol oxidation is exclusively observed if O₂ dissociates. In this case, dissociation of O₂, transfer of the hydroxyl hydrogen to one of the nascent O atoms, and transfer of one of the aliphatic hydrogens to the AuNP occurs in a concerted fashion as visualized in step b_G → c_G in Fig. 2. Analysis of the Löwdin charges during the process (Fig. 2, bottom-left panel) reveals that this complex reaction involves (i) an overall decrease of the AuNP charge, (ii) an increase of the charge of the O atoms resulting from dioxygen dissociation, (iii) an increase of the charge of the aliphatic H that is transferred to the AuNP, and (iv) a decrease of the charges of the C and hydroxyl O atoms of the reactant.

The gas phase oxidation mechanism can be rationalized as follows. O₂ gets activated because of charge transfer from the AuNP, thus causing its dissociation. At the same time, one of the resulting O atoms is able to capture the hydroxyl proton, thus forming a Ti_{5c}-O-H group, whereas one of the aliphatic hydrogens is transferred as a hydride to the AuNP, which has become slightly positively charged after charge transfer to O₂ and is now a better acceptor for the negative charge of the hydride (see reaction scheme in the top panel of Fig. 2). The gross picture of the gas phase reaction is that of a concerted charge flow process involving three actors: From methanol to the AuNP in the form of the aliphatic/hydridic H⁻ and from the AuNP to the dissociating O₂ which in turn captures the hydroxylic/acidic H⁺. Overall, this concerted dynamical process at finite temperature is consistent with the static zero-temperature perspective

of gas phase methanol oxidation obtained in terms of a sequence of separate steps. [38, 39]

Anticipating a key effect, the fundamental difference of methanol oxidation on Au/TiO₂ in liquid water with respect to the gas phase is that the reaction loses its concerted character and becomes stepwise (see supporting Section II for the interatomic distance plots where the difference is readily seen). Both, in neutral and basic water the reaction starts with the dissociation of dioxygen and thus with formation of the reactive complexes b_N and b_B in Fig. 2; note that all solvent molecules are excluded only for the sake of presentation. We note in passing that O₂ splitting appears to be more facile in basic water compared to neutral water (see supporting Section II.C for background and details). As in the gas phase, O₂ dissociation proceeds with concurrent charge transfer from the AuNP to dioxygen (see Fig. 2, bottom), the main difference being that the total charge of the cluster is higher in the liquid phase than in the gas phase by roughly 1 e⁻. This enhanced charge of the AuNP stems from its interaction with hydration shell water and, thus, is a solvation-induced charge transfer effect at thermal equilibrium conditions [35] (see Table I in the SI of Ref. [35], where the sum of the time-averaged Löwdin charges is found to be higher in the liquid than in the gas phase). This greater charge of the AuNP due to solvation enhances the activation of the O₂ molecule at the perimeter site of the catalyst, being therefore easier to dissociate in the liquid compared to the gas phase.

Once O₂ dissociates, one of the nascent oxygen atoms is able to capture the acidic hydroxyl proton. Interestingly, in the case of the reaction in neutral water this happens *via* a Grotthuss-like diffusion process involving a water molecule that accepts the hydroxyl proton and donates one of its original protons to the adsorbed O atom on the substrate (as captured by snapshot c^{tr} in Fig. 2(bottom panels), see also step b_N → c_N^{*}/c_N in Fig. 2 (top panels); additional snapshots are presented in supporting Section II.B). In both neutral and basic water, the resulting methoxy intermediate remains stable, accepting H-bonds from the surrounding waters, until its orientation is such that one of the aliphatic hydrogens is close enough to the AuNP ($\sim 2 \text{ \AA}$, structures c_N and c_B in Fig. 2). Once this happens, this particular hydrogen is transferred to the AuNP as a hydride as evidenced by the analysis of the Löwdin charges in the presence of hydration water and the synthesized formaldehyde molecule desorbs from the catalytic site. In neutral water, this final transfer occurs readily as the Au–H distance reaches about 2 Å, while at alkaline conditions there is first an interplay with the H⁻ being

shared between the methoxy and the AuNP, going transiently back and forth between them until the product is finally formed; see supporting Section II for structural analyses.

Our simulations disclose that direct methanol oxidation by activated O₂ in the aqueous phase features two important differences with respect to the gas phase reaction on the same but dry Au/TiO₂ nanocatalyst. First of all, O₂ activation is enhanced because of the greater charge of the AuNP due to its solvation compared to the analogues conditions in the absence of water, i.e. being only exposed to vacuum. Secondly, the formation of the methoxy intermediate precedes the final transfer of the hydridic H⁻ to the AuNP which ultimately yields the product, formaldehyde. It is this second aspect which makes methanol oxidation in aqueous solution particularly interesting when compared to the gas phase. In the gas phase, transient charge creation or even its local accumulation is energetically disfavored and, thus, all charge transfers are synchronized: The AuNP must transfer charge to O₂ and it must also accept the negative charge from H⁻ which are concerted events in the gas phase such that there is a “closed loop” of charge transfer (from H⁻ to Au to O₂ which accepts the H⁺). In the liquid phase, in stark contrast, these events can be readily decoupled in a high-dielectric protic solvent such as water: The enhanced charge of the solvated AuNP allows for O₂ activation without the need of accepting the H⁻ concurrently, while on the other hand the methoxy species can be formed and stabilized by the solvating waters *via* H-bonding interactions. Moreover, these events are decoupled not only *in time* but also *in space*. Indeed, the concerted closed loop character of all events in the gas phase environment requires that methanol is co-adsorbed at the same perimeter site where the oxidation agent, O₂, is located. At variance, this is not at all necessary in the presence of water since the acidic hydroxyl proton can be transferred easily *via* Grotthuss diffusion to the dissociated O atoms stemming from dioxygen. This implies that the oxidation reaction may happen whenever methanol is in contact with the AuNP in any suitable configuration that allows the transfer of one of the aliphatic hydrogens of the methyl group.

We conclude that thermal methanol oxidation by dioxygen activated at perimeter sites of Au/TiO₂ nanocatalysts is distinctly different in the liquid compared to the gas phase. Gas phase conditions are shown herein to impose concertedness in the charge transfers associated to O₂ splitting close to the AuNP and abstraction of an aliphatic hydrogen by the latter. In stark contrast, the aqueous phase reaction is a stepwise process

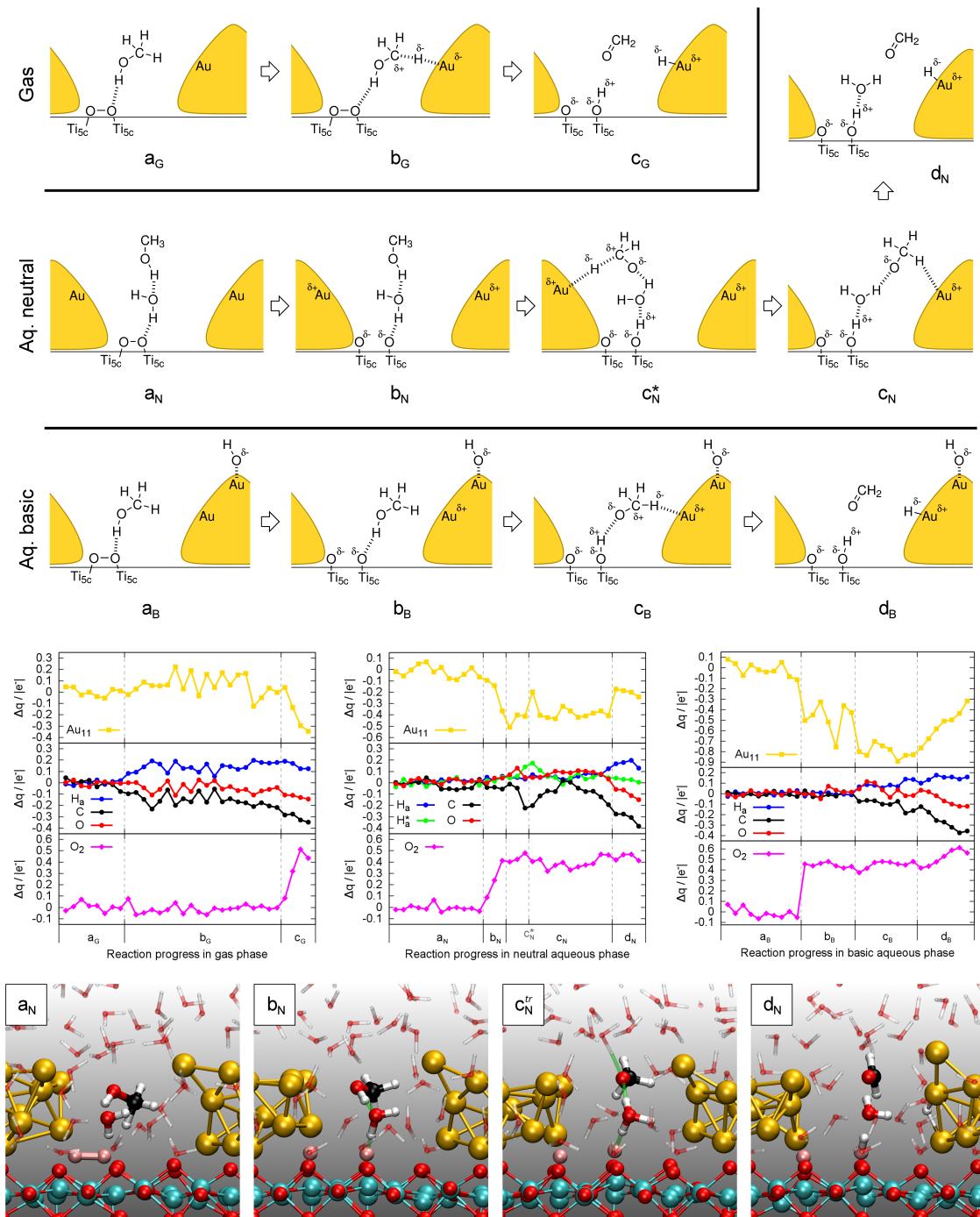


Figure 2: Top panels: Schematic reaction mechanisms for the CH_3OH oxidation on $\text{Au}/\text{TiO}_2/\text{O}_2$ in the gas phase, in neutral water and in basic water from top to bottom as extracted from the *ab initio* simulations where partial charges δ^\pm resulting from charge transfer are assigned according to the population analyses presented in the respective middle row panels (the AuNP is depicted as a golden pyramid; only the reactive water molecules involved in the two liquid-phase mechanisms are shown whereas all solvating waters, Fig. 1, are omitted). Middle panels: Evolution of the Löwdin charges of the relevant atoms as indicated in the legends along the reaction pathways of methanol oxidation to formaldehyde in the gas (left), neutral aqueous (middle) and alkaline aqueous (right) phases in terms of the charge differences relative to the reactant state; the correlation evolution of selected bond distances is shown in Fig. 1 in the SI. Bottom panels: Real-space snapshots showing representative configurations of the reaction in neutral aqueous solution corresponding to a_N , b_N , c_N^{tr} and d_N , see scheme above and text.

where these events are fully decoupled not only in time, but also in space. This is enabled by H-bonded water molecules that can easily transfer the detached hydroxyl proton, yielding a hydrated proton $\text{H}^+(\text{aq})$, *via* Grotthuss charge migration to the activated O_2 molecule. We expect our key findings to be generic and thus valid much beyond the specific case of methanol oxidation on AuNPs supported by titania, and also consider our methodological approach in the spirit of Solvation Science to be generally applicable to elucidate liquid-phase heterogeneous catalytic reactions.

Methods: Methods, model and computational details are provided in the SI.

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