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Research Note

Anticipating catalytic oxidation reactions on gold at high pressure (including liquid phase) from ultrahigh vacuum studies

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ABSTRACT

Evidence for the mechanistic link between low pressure studies and the high pressure, aqueous phase, catalytic partial oxidation reactions of ethanol on gold is provided. The oxidation of ethanol on gold (111) leads to the formation of ethyl acetate and acetic acid, as was also reported for this reaction over supported gold catalysts in aqueous phase. This reaction follows a pattern previously observed in ultrahigh vacuum on both silver and gold single crystals. The formation of both acetic acid and ethyl acetate in solution can be anticipated from prior experiments on single-crystal surfaces in ultrahigh vacuum, showing a strong parallel between the oxidation behavior of gold under these extremely different conditions. This parallel suggests that other oxidation reactions on gold may be anticipated from previous studies at low pressure and may serve as a guide for their prediction even in the liquid phase.

There has been a tremendous interest in gold-based catalysis during the past decade [1–3], with recent work focusing on the selective oxidation of alcohols—both in the gas and solution phase [4–8]. An article recently published in the *Journal of Catalysis* clearly shows the aerobic oxidation of ethanol in an aqueous solution to form both acetic acid and ethyl acetate under pressures of ca. 3.5 MPa at temperatures between 360 and 470 K [9]. In this note we provide mechanistic links for the formation of both acetic acid and ethyl acetate in aqueous solution derived from prior experiments on single-crystal surfaces in ultrahigh vacuum, which indicate that this reaction in solution follows a general pattern previously obtained from low pressure ultrahigh vacuum studies. This is an intriguing link that, when generalized, warrants further exploitation in heterogeneous catalysis by gold.

The so-called "pressure gap" has long been debated in heterogeneous catalysis [10–14]. It has mainly been directed toward gas-phase, heterogeneously catalyzed reactions, but the same arguments apply for solution reactions. The argument is that studies of reactivity under low pressure conditions typical of single-crystal studies have limited relevance to practical catalysis because practical conditions are at much higher pressure. This emphasis on pressure, however, is somewhat misplaced, especially for Au- and Ag-based catalysis.

The most important aspects of surface reactions are the identity and surface concentration of the adsorbed reactive intermediates and the reaction pathways accessible under the reaction conditions. Thus, the temperature is also a critical parameter in "catalytic reaction space" because in a complex reaction there may be competing parallel and serial processes that shift in importance with temperature. Moreover, rates increase exponentially with temperature and only (essentially) linearly with pressure. In general, catalytic reactions are conducted in practice at both higher pressures *and* temperatures than are the corresponding studies at low pressure in order to keep the surface concentration of the reacting species at an optimum fractional coverage of the surface. Thus, for similar surface concentrations of the reacting species under different pressure conditions, the surface temperature will dictate the reaction network followed.

Regardless of the conditions for which the surface reactions and their rate constants have been clearly documented, however, these reactions are relevant, and they must be considered as applicable to any conditions of P and T unless otherwise shown specifically to be irrelevant. The translation of ultrahigh vacuum studies in explaining the oxidation of methanol to formaldehyde under industrial conditions via microkinetic analysis is an excellent example of the relevance and power of fundamental surface studies in practical catalysis [15,16]. A similar lesson is learned from the applicability of fundamental studies of reactions of simple atmospheric gases, as exemplified in the calculation of the potential ozone depletion by supersonic jet exhausts in the stratosphere from basic

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kinetic data obtained in laboratory conditions [17,18]. When reactions are understood, they become a relevant base of information under all applicable conditions.

There is an abundance of mechanistic information about catalytic partial oxidation derived from surface science, particularly on silver [19], and a lesser amount on gold [20]. It is straightforward to apply some of this information, along with simple chemical analogy to draw a strong parallel between surface science studies and the mechanism of this high pressure, aqueous phase, catalytic partial oxidation reactions of ethanol on gold. Gold and silver are particularly apt bridges between fundamental ultrahigh vacuum studies on single crystals and supported catalysts because these metals are themselves rather unreactive—generally requiring activated oxygen to activate, e.g. C–H or O–H bonds.

Chemistry is a science of analogy. This is its beauty. Organic chemistry, for example, thrives on this fact and enormous advances in complex chemistry are based on this premise. As a simple example, reactions of aliphatic alcohols are discussed in general terms, focusing primarily on the hydroxyl function and only secondarily on the alkyl group. Though differences in reactivity *are* observed depending on the nature of the alkyl group, these are discussed as secondary influences, the primary functionality of the molecule being the OH group. Similar patterns of reactivity apply to surfaces; thus, surface chemistry and catalysis can also be advanced by making use of general patterns of reactivity established by fundamental studies.

The high pressure reaction that suggests this bridge is the aerobic aqueous oxidation of ethanol over gold:

$$\mathrm{CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CH_3COOH + CH_3CH_2OOCCH_3} \quad (1)$$

or, more generally,

$$\mathrm{ROH \rightarrow R'CHO \rightarrow R'COOH + ROOCR'}. \quad (2)$$

It is important to note that reactions of this type have been well documented in the partial oxidation of methanol and ethanol on silver single-crystal surfaces [21,22] and for methanol on gold single crystals [23] at low pressure. Activation of the alcohol is known to occur by a simple sequence:

$$\mathrm{O_2(g) \rightarrow 2O(a)}, \quad (3)$$

$$\mathrm{ROH(g) + O(a) \rightarrow RO(a) + OH(a)}, \quad (4)$$

$$\mathrm{ROH(g) + OH(a) \rightarrow RO(a) + H_2O}. \quad (5)$$

The same reactions would be expected to occur in aqueous phase in the presence of oxygen, as water is weakly bound to silver or gold. For example, the heat of desorption of water from Au(111) is the same as the heat of sublimation of water itself [24]. Further, if hydroxyl is the dominant surface species rather than adsorbed oxygen, reaction (5) will activate the alcohol. The important aspect of this reaction is that activated oxygen or adsorbed hydroxyl groups lead to the adsorbed alkoxide. The alkoxide intermediate is also proposed by Jorgensen et al. for the aqueous phase reaction of ethanol.

Subsequent reactions occur as follows on silver [(7), (8)] and gold [(8)] single crystals:

$$\mathrm{RO(a) \rightarrow R'CHO + H(a)}, \quad (6)$$

$$\mathrm{2H(a) \rightarrow H_2(g)} \quad (7)$$

or

$$\mathrm{RO(a) + H(a) \rightarrow ROH(g)}. \quad (8)$$

Further,

$$\mathrm{R'CHO + O(a) \rightarrow R'CHOO(a) \rightarrow R'COO(a) + H(a)}, \quad (9)$$

which can be followed by

$$\mathrm{R'COO(a) + H(a) \rightarrow R'COOH}. \quad (10)$$

Lastly,

$$\mathrm{R'CHO(a) + RO(a) \rightarrow ROOCR' + H(a)}. \quad (11)$$

All of these reactions have been well documented for the partial oxidation of *methanol* on Ag(110) [21] *and* Au(110) [23] surfaces. They occur at low to moderate temperatures, indicating that the activation barriers are modest. Most have been well documented for reactions of *ethanol* on Ag(110) [22]. Every reaction necessary to understand the reaction products observed in the aqueous process reported by Jorgensen et al. [9] has been documented on silver single crystals under ultrahigh vacuum, and analogous reactions have been shown to occur on gold single crystals. The fact that in the Jorgensen studies more ester is produced as the concentration of ethanol in the solution is increased also agrees with the prediction of this mechanism derived from low pressure studies.

The analogy between the surface reactions observed on single crystal surfaces of silver to reactions on gold is potentially much broader. The extension of the patterns of reactivity on silver surfaces to gold surfaces was previously examined by Outka et al. [23]. They state that the results of their studies on Au(110) "strongly suggest that a whole range of similar reactions that have been observed on copper and silver surfaces will occur on gold surfaces. Thus oxygen adatoms are expected to promote reactions with alcohols, terminal acetylides, carboxylic acids, water and other gas phase Brønsted acids. Oxygen is also expected to promote reactions containing nucleophilic centers such as: aldehydes, esters, sulfur dioxide, etc." Thus, the applicability of the ultrahigh vacuum studies to partial oxidation on gold is potentially even broader than just for the types of reactions reported by Jorgensen et al. For example, oxygen adsorbed on silver is known to selectively attack gas-phase acidic bonds in a variety of organic molecules, including alkenes [25,26], nitriles [27], acetylides [28], etc., and some reactions of this type have recently been discovered on gold single-crystal surfaces [29,30].

To test our assertion that the reactions observed in water could have been anticipated on the basis of the earlier low pressure studies on silver and gold single crystals, we specifically examined the oxidation of ethanol to ethyl acetate and acetic acid on gold (Fig. 1). Standard UHV procedures, described in detail previously [29], were used. Gold(111) surfaces were precovered with atomic oxygen by decomposition of O_3 at 200 K and subsequently exposed to ethanol. At an initial oxygen coverage of 0.4 ML ethyl acetate forms below 250 K, and acetic acid evolves from the surface at temperatures of 450 and 545 K (Fig. 1). In addition, ketene is formed. The expectations of the formation of ethyl acetate and acetic acid in the oxidation of ethanol on Au(111), based on prior results from ultrahigh vacuum studies of methanol and ethanol oxidation on silver and gold single-crystal surfaces, *are* realized. Furthermore, the fact that these reactions occur similarly on both Au(110) and Au(111) surfaces indicates that they are not structure sensitive and mitigates against the necessity for particular site geometries for reactions (6)–(11) above. Moreover, the yield of ethyl acetate greatly increases when acetaldehyde is co-dosed onto the surface (data not shown), providing further evidence that its formation follows the mechanism as described in reaction (11). Finally, this mechanistic explanation indicates that the selectivity for production of ethyl acetate can be manipulated by adjusting the reactions conditions, e.g., the ethanol/oxygen ratio. The yield of ethyl acetate increases for high ethanol/oxygen ratios and further increases when acetaldehyde is co-adsorbed with the ethanol on oxidized Au(111). The reported increase in the production of ethyl acetate in ethanol oxidation over supported Au in aqueous

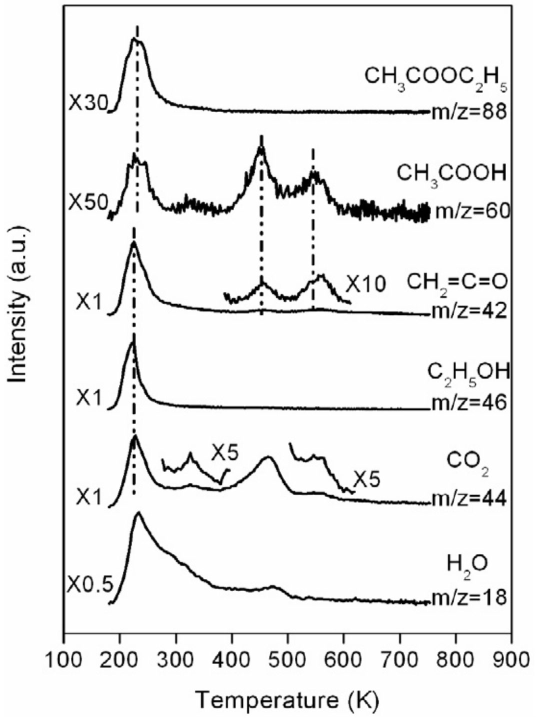

Fig. 1. Temperature programmed reaction spectra of the oxidation of ethanol on the Au(111) surface. The surface is pre-covered with oxygen adatoms with a coverage of 0.4 ML. The dash–dot lines denote the fragment peaks that align with their corresponding parent ion peaks.

solution, indeed, parallels our observations under UHV conditions on single-crystal surfaces.

Furthermore, important information is known about the effect of excess surface oxygen on these reactions which underscores their importance at the temperatures and pressures of the aqueous solution studies. In general, excess adsorbed oxygen, which might be expected under conditions of higher pressure, converts adsorbed acetate intermediates into formate, promoting its decomposition to CO_2 well below its temperature for decomposition, were it adsorbed alone [31], and providing a clean source of hydrogen. Factors such as this may serve to increase the rates of the reactions of adsorbed acetate, shifting them well into the temperature range used in these high pressure aqueous reactions.

Gaining a mechanistic understanding from single-crystal studies overall is important in understanding and controlling the factors that determine reaction selectivity. In the paper by Jorgensen et al. [9], they presented a phenomenological mechanistic model. In their model they asserted that ethanol is converted into ethoxy which then is transformed in turn into acetaldehyde and acetic acid. The formation of ethoxy exactly parallels the previous studies under ultrahigh vacuum [22,32] and in heterogeneous catalysis [33]. The formation of acetaldehyde, acetic acid and ethyl acetate may be explained by the reactions detailed above, elucidated by previous UHV work. More difficult is the mechanism of CO_2 production. In the ultrahigh vacuum studies the primary route to CO_2 production is via acetate, which also would lead to acetic acid production, given a source of hydrogen or protons. In the UHV experiment for ethanol oxidation reported here acetate disproportionates to acetic acid and ketene (Fig. 1). Since no ketene is reported in the Jorgensen work, in aqueous solution another source of protons must be available for the formation of acetic acid—one likely source is the surrounding aqueous medium. As noted above, this source could also be formate, derived from oxygen attack on adsorbed acetate. This difference in detail of the manner of formation of acetic acid from acetate remains to be resolved.

A second important point concerns the activation of oxygen and the mechanism of the activation of the alcohol to ethoxy, steps (3)–(5). While there is debate regarding the possibility that molecular oxygen directly participates in oxidation catalysis on Au, it is clear that atomic oxygen is very active for these reactions, including the initial activation of ethanol to form ethoxy. Such reactivity remains to be shown for adsorbed dioxygen. Molecular oxygen is extremely weakly bound on Au, desorbing at 45 K and its activation on clean single-crystal gold surfaces has not been observed. Dioxygen has, however, been successfully employed in gold catalyzed oxidation of hydrocarbons and CO oxidation, so there must be a mechanism for its activation [34]. On the other hand, O_2 has been dissociated over a morphologically rough Au(111) surface seeded with adsorbed atomic oxygen [35] and in the presence of migrating Au adatoms on the Au(111) surface [36]. While it is not the purpose of this paper to address the issue of whether adsorbed atomic or molecular oxygen is the oxidant, we clearly have observed the same general pattern of reactivity for ethanol oxidation with atomic oxygen on the Au surface as observed in aerobic aqueous solution. Further, notably, we have previously shown that the O-covered Au(111) surface is morphologically rough, thus, qualitatively resembling the Au nanoparticles on the metal oxide supports [37].

It may be relevant that the same controversy regarding oxygen activation remained at issue for decades in the epoxidation of ethylene on silver until it was shown definitively that adsorbed atomic oxygen epoxidized olefins without allylic C–H bonds. Nonetheless, it is clear from the results of Jorgensen et al. that the results of the earlier fundamental ultrahigh vacuum studies parallel the more recent results of the aerobic catalytic oxidation of ethanol over gold and are clearly relevant for the understanding of catalytic reactions such as these.

Although we specifically focus on the example of ethanol oxidation on Au catalysts herein, the same arguments apply to many other systems of interest in catalytic chemistry, especially oxidation reactions on coinage metals. Previous studies of the kinetics and mechanism of partial oxidation reactions on coinage metals clearly have relevance to reactions at higher pressure. The wealth of this mechanistic information, established in detail for molecular rearrangements particularly on silver and gold single-crystal surfaces, can serve as a valuable guide for *predicting* reaction processes under vastly different conditions.

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