

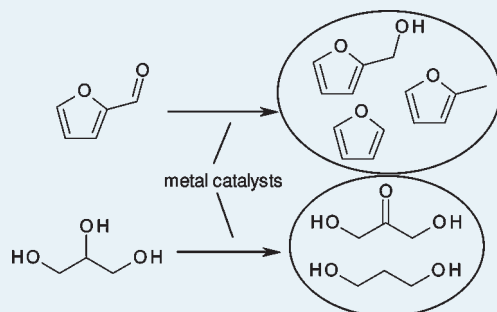
Understanding and Controlling Reactivity of Unsaturated Oxygenates and Polyols on Metal Catalysts

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ABSTRACT: The production of fuels and chemicals from biomass requires heterogeneous catalysts that facilitate selective reactions of highly functional oxygenates. Although designing catalysts for high selectivity is a universal challenge in heterogeneous catalysis research, the problem is particularly acute for highly functional molecules, which contain two or more functional groups that may react over metal surfaces. This perspective article focuses on recent efforts to develop structure–property relations on metal surfaces and catalysts for two classes of highly functional molecules: multifunctional oxygenates such as α,β -unsaturated aldehydes and furanic compounds, and polyfunctional oxygenates such as glycerol and other polyols. Recent results from comparative reaction studies over a variety of catalysts, surface science experiments, and computational investigations suggest an array of approaches for producing more selective catalysts, many relying on the addition of multiple metals or other surface modifiers. General strategies that appear to show promise in the selective reactions of unsaturated oxygenates and of polyols are discussed in detail.

KEYWORDS: cellulosic biomass, biorefinery, alcohol oxidation, aldehyde hydrogenation, platinum, gold, palladium, ruthenium



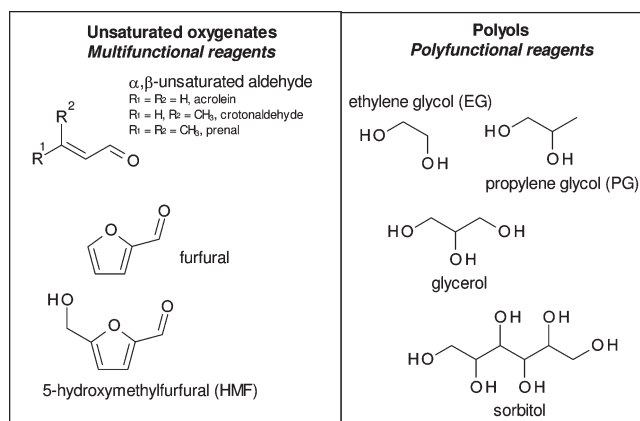
1. INTRODUCTION

The interest in conversion of biomass to fuels and chemicals has driven renewed emphasis on developing heterogeneous catalysts for reactions involving oxygenated compounds. A number of useful platform chemicals can be produced from biomass deconstruction, as discussed in several recent reviews.^{1,2} Many of these chemicals are highly functional oxygenates; that is, they contain two or more functional groups, at least one of which is an oxygen-containing function. The production of an array of useful chemicals and fuels from these platform chemicals in a biorefinery requires the capability to selectively catalyze targeted transformations at a particular functional position on the molecule. Producing supported metal catalysts capable of such selective transformations is a challenging objective, because highly functional oxygenates can potentially bind to the catalyst and react through any of their functional groups. Thus, the design of catalysts that are selective for reactions of multifunctional oxygenates is even more complex than for reactions of monofunctional compounds, already a major focus of heterogeneous catalysis research.

The surface chemistry of simple oxygenates on catalytically active metal surfaces has previously been reviewed.³ This perspective article focuses on recent attempts to identify active and selective metal catalysts for transformations of several probe reactions involving highly functional oxygenates. These reactions are divided into two fundamental types, as illustrated in Scheme 1:

- (1) Reactions of *multifunctional* compounds. As defined in this perspective article, multifunctional molecules include combinations of diverse functional groups, for example, the aldehyde, ether, and C=C unsaturated

Scheme 1. Examples of Multifunctional and Polyfunctional Oxygenates Considered in This Article



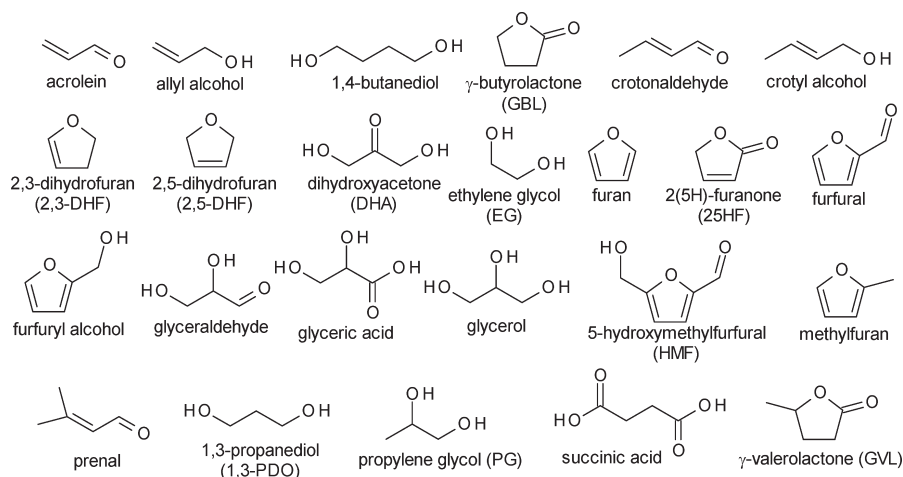
functions in furfural. Because of substantial chemical differences in the functional groups, there seems to be a strong opportunity for development of catalysts that are specific for reactions of particular functional groups. For example, one can envision bifunctional catalysts in which an oxygenated function interacts with one metal and an olefin function with another.^{4,5} Such ideas have in fact served as significant drivers for research into the

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Scheme 2. Molecular Structure of Key Compounds Discussed in This Article, Organized Alphabetically



hydrogenation of α,β -unsaturated aldehydes (perhaps the most investigated multifunctional reagents). However, as discussed below, simplified notions about bifunctional catalysts for reactions of unsaturated aldehydes have been called into question based on recent research. These issues are likely to be important in reactions of furanic compounds derived from biomass, as also discussed below.

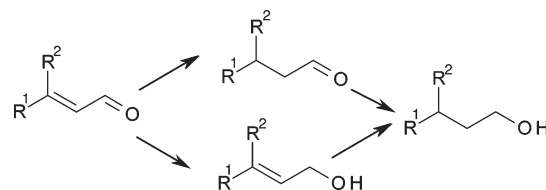
- (2) Reactions of *polyfunctional* compounds. Polyfunctional compounds, as defined in this perspective article, contain multiple occurrences of the same functional group. One classic example of such a class of compounds, and the focus of this article, is the polyols. Commonly referred to as “alcohol sugars”, polyols such as glycerol ($C_3H_5(OH)_3$), xylitol ($C_5H_7(OH)_5$), and sorbitol ($C_6H_8(OH)_6$) are key intermediates in biorefining pathways.⁶ Selective conversions of polyols into desired products, for example, through oxidation to hydroxylated aldehydes, ketones, and acids or hydrogenolysis to lower molecular weight polyols requires a high degree of reaction specificity. As discussed below, it is often desirable to control reaction selectivity toward conversion of primary versus secondary alcohols. Given the uniformity of the functional groups, achieving such specificity represents a very difficult objective for heterogeneous catalysis by metals.

Below, we describe efforts to understand the reaction chemistry of highly functional oxygenates on heterogeneous metal catalysts and to develop improved catalysts for biorefining and other applications. Scheme 2 presents the molecular structures for key compounds discussed in these sections. Surface-level investigations of the relevant chemistry are described, focusing on how the presence of multiple functional groups affects adsorption and reaction behavior on transition metal surfaces. Structure–activity relations determined from reaction investigations over a variety of supported catalysts are also discussed. Finally, we attempt to outline general trends that are potentially important in the design of selective heterogeneous catalysts.

2. REACTIONS OF MULTIFUNCTIONAL MOLECULES

The reactions of oxygenates with unsaturated C=C or aromatic functions are of key importance for a number of biorefining

Scheme 3. Principal Reaction Paths of α,β -Unsaturated Aldehydes during Hydrogenation over Pt Group Catalysts



reactions. The thermal treatment of lignin can produce a range of aromatic oxygenates that can be refined for production of fuel components and chemicals.⁷ A variety of unsaturated oxygenates can also be produced from cellulosic biomass; the focus of much of the discussion below is on furanic compounds such as furfural and 5-hydroxymethylfurfural, proposed as key building blocks for biorefining. In the following sections, we begin by discussing previous studies of α,β -unsaturated aldehydes as a model system for reactions of unsaturated oxygenates. We then focus on investigations of furanic compounds that have greater direct relevance for biorefining routes.

2.1. Hydrogenation of α,β -Unsaturated Oxygenates. The selective hydrogenation of unsaturated aldehydes such as acrolein, crotonaldehyde, and prenal to unsaturated alcohols has been a major focus of catalysis research for decades, and the chemistry has been the subject of extensive reviews.^{8–12} We will therefore focus primarily on recent surface-level investigations of this chemistry. See Scheme 3 for a summary of the basic reaction paths. In general, over typical hydrogenation catalysts such as supported Pt and Pd, selectivity to the saturated aldehyde is much higher than the unsaturated alcohol, while at high conversion the fully saturated alcohol is formed.¹³ The selectivity toward the unsaturated alcohol increases with methyl substitution, so that prenal hydrogenation is significantly more selective than acrolein hydrogenation.¹¹ Supported Pt and Pd catalysts are well-known for their activity for binding and hydrogenating olefins, so this affinity for olefin hydrogenation might be interpreted in terms of an adsorption geometry that favors binding of the olefin over binding of the aldehyde function. However, the situation is somewhat more complicated.

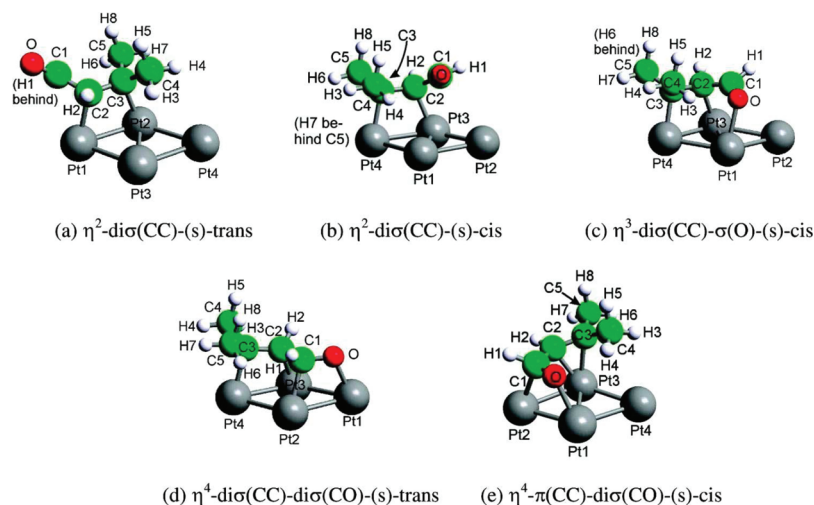


Figure 1. Adsorption modes of prenal on Pt(111) identified from a combination of density functional theory calculations and vibrational spectroscopy. Adsorption energies in kJ/mol for each structure were reported as (a) -54.2 , (b) -47.8 , (c) -49.5 , (d) -58.6 , and (e) -47.2 . Reprinted from ref 29. Copyright 2008 American Chemical Society.

Before discussing the surface chemistry of α,β -unsaturated aldehydes, it is useful to very briefly review the results of previous surface science studies of simple aldehydes (such as acet-aldehyde) and alkenes (such as ethylene) on Pt-group surfaces. On these surfaces, two basic adsorption geometries are commonly observed: an η^1 configuration in which the aldehyde is bound through the O lone pair, and an η^2 configuration in which both the C and the O atoms of the carbonyl function are bound to the surface, resulting in significant rehybridization of the C–O bond.^{14–19} The more strongly adsorbed η^2 carbonyl species typically react on transition metal surfaces via C–H scission at the carbonyl position and subsequent CO abstraction; on some surfaces, the decarbonylation reaction appears to be preceded by dehydrogenation at the β -C position which competes with C–O scission.¹⁸ Ethylene can also adsorb in at least two configurations: through an interaction of the ethylene π electrons with the surface or through formation of σ bonds with each of the carbon atoms. The di- σ state is typically more stable, while the π state is the more reactive species for ethylene hydrogenation.^{20,21} Adsorbed ethylene can also undergo dehydrogenation-rehydrogenation to produce highly stable ethylidyne intermediates.

Experimental studies on single crystal surfaces of Pt^{22–24} and Pd^{25–27} have shown that α,β -unsaturated aldehydes generally adopt a flat-lying adsorption geometry at low coverages, such that both the olefin and the aldehyde functional groups coordinate with the surface. However, the detailed surface chemistry is highly dependent on the adsorbate coverage, and the molecular structure of the α,β -unsaturated aldehyde. For example, the presence of a methyl group in crotonaldehyde causes significant differences both in preferred binding geometry and in observed thermal decomposition products on Pd(111) and Pt(111) that seem unexpected given the weak interaction strength between methyl groups and the surface.^{23,26,27} While initial attempts to identify binding geometries of unsaturated aldehydes focused on determining a single “most preferred” structure, recent studies employing both surface science experiments and density functional calculations indicate that the adsorption chemistry of unsaturated aldehydes is highly complex. Multiple intermediates having different degrees of coordination—from relatively upright adsorbates bound through one of the two functional groups, to

flat-lying adsorbates—exist on the surface.^{28–35} Figure 1 shows the example of prenal adsorption on Pt(111), where at least five adsorbed forms are detected on the surface after adsorption at low temperature.²⁹ The most highly coordinated (η^4) forms of the molecule are populated at low coverage, with less-coordinated states becoming more prevalent at higher adsorbate coverage. As several previous studies have shown, the more weakly adsorbed species formed at higher coverages are often expected to be most important under conditions of catalysis.^{20,21,36}

Recent work by Loffreda et al. has challenged the assumption that the lower selectivities to unsaturated alcohols over Pt surfaces are a direct result of preferential binding and faster reaction for the olefin function. They found that the elementary C=O hydrogenation step is actually more rapid, even when the molecules are bound through the C=C function.³⁷ The C=O hydrogenation reaction proceeds through a metastable precursor state for O–H bond formation where the O is not directly bound to the surface, with the α,β -unsaturated aldehyde adsorbed in a state similar to that shown in Figure 1(a). This reaction involves a surface-bound H atom and an O atom that is not directly adsorbed on the surface but is in proximity because of the adsorption of the C=C function. It was thus described as being intermediate behavior between Langmuir–Hinshelwood and Eley–Rideal type adsorption and reaction. In contrast, olefin hydrogenation, which occurs through the adsorbed C=C function, is purely a Langmuir–Hinshelwood process. The higher activation energy for desorption of the unsaturated alcohol product from the surface was determined as the reason for lower selectivity observed for this pathway. Thus, tight binding of the olefin plays a role in suppressing selectivity to the desired product, but in a more indirect way than perhaps commonly envisioned. In this view, the tight binding of the olefin function in the desired product limits selectivity to the unsaturated alcohol not because of faster reaction of the more strongly adsorbed functional group, but because tighter binding of that functional group inhibits desired product desorption.

Ultimately, it is desirable to use insights from fundamental investigations to design new catalysts for unsaturated oxygenates. Loffreda et al. have recently demonstrated that selectivity predictions can be made on a simplified basis by constructing

Brønsted–Evans–Polanyi (BEP) relations to determine the activation energy of different steps in a complex mechanism.³⁸ In this approach, a linear relationship between reaction energies and reaction barriers is assumed for related reaction steps. In the case of crotonaldehyde hydrogenation, the adsorption energy of the transition state was found to be closely correlated with the adsorption energy for the hydrogenation precursor (in which the adsorbate is located in a prereaction condition next to H) when the reaction steps were placed in one of three categories. These categories were defined based on where the H atom was added: reaction with O, reaction with the aldehydic carbon, or reaction with an olefinic carbon. The same BEP relations were usable between acrolein and prenal on Pt(111), and predicted the improved selectivity for prenal hydrogenation compared to acrolein hydrogenation on Pt surfaces. This approach may therefore be useful in predicting new surface compositions that are highly selective for hydrogenation of unsaturated aldehydes. In another interesting recent contribution, Haubrich et al. have shown that the adsorption energy of unsaturated aldehydes on Pt(111) is a poor metric for describing the strength of the chemical bonds formed between the adsorbates and metal surfaces.³⁹ In some cases, strong adsorption of multiple functional groups causes significant (endothermic) relaxation of the metal surface, so that greater bond adsorbate–surface bond strengths (associated with significant rehybridization of bonds in the adsorbate) do not necessarily correlate with the overall adsorption energy of multifunctional molecules.

One method of modifying Pt-group surfaces involves the addition of oxophilic metals such as Sn and Fe.^{40,41} Such catalysts have been known for many years to improve selectivity to the desired unsaturated alcohol products. It might be supposed that the role of an oxophilic modifier such as Sn is to interact preferentially with the O atom of the aldehyde function, thus increasing the selectivity to aldehyde hydrogenation because of a stronger interaction of C=O with the surfaces. However, recent experimental and computational investigations conducted using model systems have suggested alternative functions of the modifiers.^{28,29,42,43} One of the effects of Sn in Pt₂Sn or Pt₃Sn surface alloys appears to be a general weakening of the adsorption of unsaturated aldehydes to η^1 or η^2 rather than η^4 adsorption modes that are prevalent on Pt(111), with the O atom generally interacting with the Sn atom. On Sn-modified surfaces, adsorption of crotonaldehyde through η^2 binding of the C=C function is still found to be preferred over adsorption of the C=O function; however, as discussed above, weakened binding through this function may lead to enhanced selectivity even if the carbonyl is not adsorbed, by reducing the desorption energy of the desired unsaturated alcohol product. This mechanism also explains the higher selectivity toward carbonyl hydrogenation observed for substituted α,β -unsaturated aldehydes such as prenal compared to unsubstituted acrolein. Methyl substitution at the olefin position weakens adsorption of the olefin function, improving selectivity toward the desired product.⁴⁴

Chen and co-workers have investigated a variety of Pt-based bimetallic surfaces for acrolein hydrogenation. They recently reported the observation of propenol formation from acrolein hydrogenation in ultrahigh vacuum during temperature programmed desorption (TPD) over a Pt/Ni/Pt(111) surface.⁴⁵ For this surface, Ni preferentially populates first subsurface layer, while Pt forms the surface layer. The subsurface Ni layer weakens the binding energy of acrolein and other adsorbates on the surface, and disfavors adsorption of acrolein in a strongly

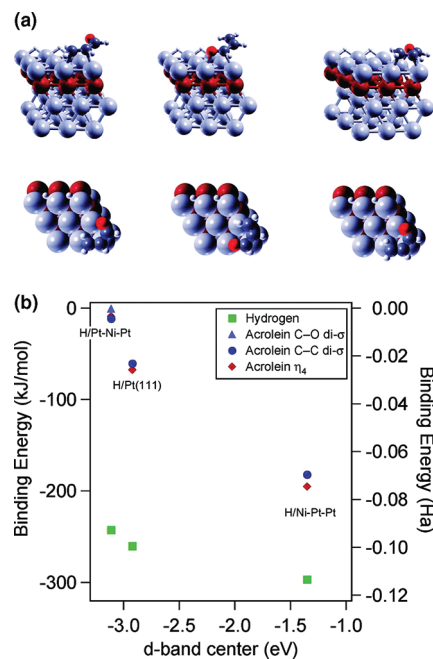


Figure 2. Adsorption modes of acrolein on Pt(111) and Ni–Pt(111) bimetallic surfaces. Subsurface Ni destabilized the adsorption of acrolein and increases the favorability of η^2 -adsorption of the aldehyde function (left figure in part (a)) compared to adsorption of the olefin function or η^4 adsorption (through both functions center and right structures in (a)). Reprinted from ref 45. Copyright 2007 American Chemical Society.

coordinated η^4 configuration.^{46,47} Adsorption of the aldehyde function was observed to become energetically competitive with (but still weaker than) the C=C function for the Pt/Ni/Pt(111) surface, as shown in Figure 2. On the other hand, a Ni/Pt(111) bimetallic surface was found to be highly favorable toward adsorption of acrolein in an η^4 configuration, and no propenol was produced during TPD. The tendency for formation of propenol was related to the d-band center of the surface, with the Pt/Ni/Pt(111) surface having the most negative d-band center among the group Pt/Ni/Pt(111), Pt(111), and Ni/Pt(111). It was also determined that the surface concentration of coadsorbed H atoms played a major role on selectivity and on the adsorbed structure of acrolein, with the H-covered Pt/Ni/Pt(111) surface preferentially stabilizing adsorption through the carbonyl. Chen and co-workers have recently extended these studies to other Pt-3d bimetallics, including Pt/Co/Pt(111) and Pt/Cu/Pt(111). These surfaces also showed enhanced propenol production compared to Pt(111), though propenol production was higher on Pt/Ni/Pt(111) for reasons which are not currently clear.⁴⁸ Overall, these investigations suggest that a strategy of using 3d metals to weaken the binding energy of unsaturated aldehyde on Pt group surfaces can promote selectivity.

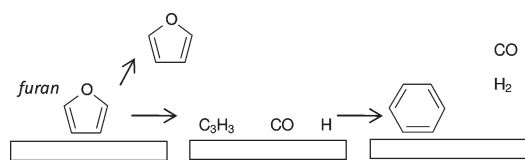
In an alternative approach to controlling selectivity, Hutchings and co-workers have observed that the selectivity for the hydrogenation of crotonaldehyde to crotyl alcohol (2-buten-1-ol) can be promoted by the addition of small amounts of thiophene to a supported Cu catalyst prior to use.⁴⁹ As thiophene was added in increasing amounts to the surface, the conversion of crotonaldehyde continuously dropped, but the selectivity to crotyl alcohol over butanol increased significantly before declining at large thiophene exposures. This effect was observed for a variety of sulfur-containing compounds.⁵⁰ More recently Chiu et al. have

studied the effect of sulfur using surface science techniques and Cu(111) single crystals.⁵¹ They observed that the addition of 0.43 monolayers of sulfur resulted in significant hydrogenation of crotonaldehyde to both crotyl alcohol and *n*-butanal during TPD with coadsorbed hydrogen, whereas hydrogenation products were absent when S was not coadsorbed. Spectroscopic techniques were used to show that sulfur modifies the electronic structure of the surface to favor tilting of the C=C and C=O bonds with respect to the surface plane, weakening adsorption and favoring hydrogenation.⁵² The C=C bond was proposed to be tilted to a greater extent than the C=O bond, favoring hydrogenation to crotyl alcohol. The continuous addition of small quantities of thiophene has also been observed to improve the overall activity and selectivity for hydrogenation of the carbonyl function of citral.³⁹ However, this effect of sulfur does not necessarily appear to be extendable to Pt-group catalysts. In related studies, Marshall et al. have recently shown that the modification of Pd/Al₂O₃ with self-assembled monolayers of alkanethiols dramatically increases the selectivity for crotonaldehyde hydrogenation to butyraldehyde, suppressing the series hydrogenation to butanol.⁵³ However, the selectivity to crotyl alcohol is not noticeably improved.

The hydrogenation of unsaturated aldehydes has also been investigated over nanoparticle Au catalysts modified by indium. Mohr et al.⁵⁴ have shown that the selectivity for formation of propenol improves upon the addition of indium to the catalyst. This has been attributed to the preference of In for being located on Au faces rather than edges; indium has been proposed to block the adsorption of acrolein on the less-selective faces, enabling the more-selective edges to participate in the reaction. However, recent theoretical calculations have challenged this interpretation. He et al.⁵⁵ used density functional theory (DFT) calculations to explore acrolein binding and hydrogenation on Au surfaces modified with In. Although their results confirmed that indium prefers to bind in the higher-coordination terrace sites, they found that C=C hydrogenation occurs preferentially at edge sites. Their calculations indicate that the presence of In promotes the adsorption of the carbonyl function of acrolein, improving the reactivity of the face sites for the desired reaction. Grass et al. recently observed that the selectivity to unsaturated alcohols is improved on supported Pt catalysts with larger crystallites and therefore relatively fewer edge sites, suggesting a similar structure sensitivity.¹³ Moreover, the structure sensitivity associated with these reactions suggests that catalyst particles with well-defined shapes, such as those increasingly employed for other catalytic reactions,^{56,57} may be a promising approach for improving selectivity in hydrogenation of unsaturated oxygenates.

Finally, a recent study by Brandt et al. focused on characterizing the relationship between acrolein adsorption geometry and hydrogenation selectivity on Ag(111).⁵⁸ At low coverages, acrolein was found to adsorb in a flat-lying geometry, but the C=C bond was determined to tilt at high coverages, leading to higher selectivity for production of the unsaturated alcohol during temperature programmed reaction. Interestingly, formation of the series reaction product propanol was controlled in part by the coverage of adsorbed H atoms, with lower H coverages leading to reduced affinity of the C=C bond in allyl alcohol for the surface and therefore reduced production of the undesired series product. It should be noted that caution must be taken when comparing the results of surface science investigations directly to high-pressure investigations using supported

Scheme 4. Furan Thermal Decomposition Pathway on Pd(111)



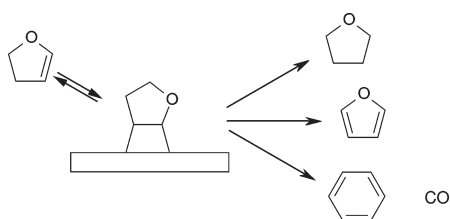
catalysts. As shown by Bron et al., the selectivity for acrolein hydrogenation to allyl alcohol on supported Ag catalysts and at high pressure is much higher than for single Ag crystals and low pressure.⁵⁹ Thus, the use of techniques such as sum-frequency generation vibrational spectroscopy for characterization of the reaction chemistry in situ will be valuable for future efforts at catalyst design. Somorjai and co-workers have recently shown that such an approach can be used to track η^2 versus η^3 forms of adsorbed unsaturated aldehydes on single-crystal Pt surfaces under relatively high pressure conditions.⁶⁰

2.2. Hydrogenation of Biomass-Derived Furanic Compounds. Functionalized furans including furfural and 5-hydroxymethylfurfural (HMF) have been proposed as compounds that will play a central role in biorefineries.⁶¹ These chemicals are produced from dehydration of C5 and C6 sugars, respectively, and performing chemistry on their functional groups provides routes to chemicals and fuels.⁶² As discussed below, there are many parallels between the surface chemistry of α,β -unsaturated aldehydes and these furanic compounds. In both cases, reaction selectivity can potentially be directed either toward an aldehyde function or an unsaturated group, and the competition for binding of these groups to the surface will hypothetically play a role in controlling selectivity. However, the furyl group presents a bulkier and even more electron-delocalized system that can affect the chemistry of the oxygenate function. Furthermore, the ether function in the furan ring can potentially play a distinct role in the chemistry.

It is first useful to review previous investigations of the surface chemistry of furan on the surfaces of traditional hydrogenation catalysts. For example, furan adsorption and decomposition has been investigated extensively on Pd(111) (Scheme 4).^{63–67} Furan adsorbs with its four carbon atoms in a plane parallel to the surface, with the O atom tilted away from the surface. During TPD, furan desorbs from a chemisorbed state just below 300 K or reacts via ring-opening decarbonylation to produce CO and C₃H₃ intermediates. The C₃H₃ intermediates can undergo subsequent coupling at higher temperatures to produce adsorbed benzene.

During hydrogenation reactions of interest for biorefining chemistry, the furan ring is expected to sequentially produce a dihydrofuran (DHF), namely, 2,3-DHF or 2,5-DHF depending on the position of the ring to which the H atoms are added, followed by tetrahydrofuran (THF). The chemistry of these compounds has also been investigated on Pd(111).⁶⁸ There are some broad similarities between 2,5-DHF and 2,3-DHF (Scheme 5) when comparing their adsorption and decomposition mechanisms.⁶⁸ Vibrational spectroscopy and DFT calculations indicate that 2,3-DHF and 2,5-DHF adsorb on Pd(111) primarily via their respective olefin functional groups at low temperature (<170 K). Both molecules undergo dehydrogenation by 248 K to form species that produce furan in a reaction-limited process above 300 K. However, there are some

Scheme 5. Thermal Decomposition Pathway of 2,3-DHF on Pd(111)^a

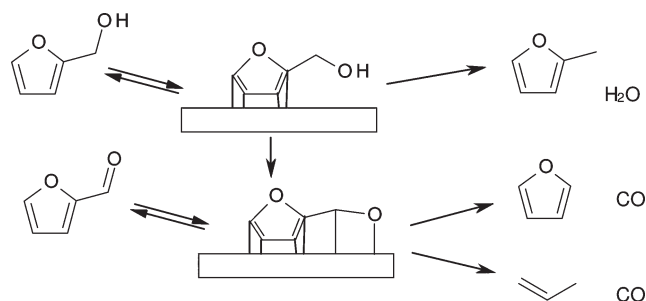


^a For simplicity, surface H atoms and H₂ are not shown.

key differences in the reactivity of these two species that are potentially important for catalysis. The first is that the position of the olefin function in the ring affects the adsorption energy C–H bond strength of adsorbed furanic compounds. It was found during TPD investigations that 2,3-DHF can be hydrogenated to produce tetrahydrofuran (THF) at about 330 K, whereas 2,5-DHF is more likely to dehydrogenate, producing furan in an additional low-temperature channel at approximately 320 K. The differences were related to differences in the reactivity of C–H bonds at the 2,5-positions compared to the 2,3-positions, that is, their proximity to the ether O atom. The proximity of the O atom to the olefin function in 2,3-DHF was also found to lead to stronger adsorption compared to 2,5-DHF.^{69,70} A second interesting observation is that in the lowest-energy pathway for production of furan, 2,5-DHF was found to incorporate deuterium atoms that were preadsorbed on the surface. Even though the production of furan from 2,5-DHF involves the net loss of two H atoms, the reaction proceeds through an intermediate that incorporates H atoms available on the surface, indicating significant C–H scission activity. In contrast, no H exchange with the surface is seen during furan TPD. As discussed in further detail below, this observation is consistent with a higher barrier for C–H scission from furan because of its aromaticity; “breaking” the aromaticity can thus lead to new surface chemistry.

More recently, the thermal chemistry of furfural, C₄H₃(CHO)O, and furfuryl alcohol, C₄H₃(CH₂OH)O, have been investigated on Pd(111), with the reported mechanism summarized in Scheme 6.⁷¹ The TPD results indicate furfural undergoes decomposition to produce furan, propylene, carbon monoxide, and hydrogen. Furfuryl alcohol forms the same products but also undergoes C–O scission to yield methylfuran and water. Together with DFT calculations, these results indicate that furfuryl alcohol can decompose through a surface furfural intermediate, similar to the reaction pathway observed for simple alcohols such as ethanol (see Section 3 below). The additional methylfuran pathway, however, is not observed for simple alcohols such as ethanol. The reactivity of furfuryl alcohol toward methylfuran formation is likely a function of the weaker C–O bond strength in furfural. The presence of the aldehyde group on the furfural furan ring also has surprising effects on reactivity of the ring. Decarbonylation of furfural produces surface furyl (C₄H₃O) intermediates that might be expected to exhibit similar chemistry to those produced from furan (C₄H₄O). However, the reaction products differ significantly. Although furan is produced during furfural and furfuryl alcohol TPD, it is found to incorporate up to two hydrogen atoms from the surface, suggesting that an additional C–H bond is broken during formation of furan from a furyl group. Furthermore, a relatively hydrogen-rich product,

Scheme 6. Furfuryl Alcohol and Furfural Thermal Decomposition Pathway on Pd(111)^a



^a For simplicity, hydrogen is not directly shown in the mechanism.

propylene, is formed even though the furyl ring itself is more hydrogen-poor than furan. The incorporation of up to five D atoms in propylene produced during furfural TPD indicates dramatic rearrangement of C–H bonds that appears to be facilitated on furyl compared to furan. Thus, the chemistry of substituted and unsubstituted furans can differ strongly; substituent groups such as carbonyl ligands that can dissociate from the furan ring create furyl intermediates that have lower symmetry/aromaticity compared to furan, changing the slate of reaction products.

These pathways are also observed in the reactivity of furanic compounds over supported Pd catalysts under higher-pressure reaction conditions. For example, Zhang et al.⁷² investigated unmodified and K-modified Pd catalysts for the decarbonylation of furfural in the presence of hydrogen. As expected from the model studies described above, where decarbonylation was the major pathway, selectivity to CO and furan was observed to be high on Pd catalysts. The main nonselective product is methylfuran, hypothetically formed by hydrogenation/hydrogenolysis of the C=O bond. These pathways mirror those observed on the Pd(111) surface in UHV experiments (Scheme 6) suggesting that surface-level studies can provide insights into reaction mechanisms and the design of improved catalysts for reactions of furfural. Interestingly, K-promoted catalysts were found to exhibit improved selectivity to decarbonylation relative to hydrogenolysis to methylfuran. This was hypothesized to be due to a weakened interaction of the η² aldehyde, and based on other work could perhaps be related to the preferential alignment of the CHO dipole to favor C–C scission at the surface.^{73,74}

Further insights are available by considering analogies with the reactions of unsaturated aldehydes such as acrolein, crotonaldehyde, and prenal. As noted above, the furyl group in furfural is expected to play a similar role in modifying the reactivity of the aldehyde as the olefin function of α,β-unsaturated carbonyl compounds. Therefore, the same approaches for modifying catalytic activity and selectivity may be available for reactivity of furanic compounds. Merlo et al.⁷⁵ investigated the hydrogenation of furfural over PtSn bimetallic catalysts with similar compositions to those employed for saturation of α,β-unsaturated aldehydes. They observed improved rates for Sn-modified catalysts, with a maximum rate observed for PtSn_{0.3} catalyst that was approximately six times higher than a pure Pt catalyst. The selectivity to furfuryl alcohol was high (>96%) regardless of Sn content. The rate enhancement observed is consistent with weaker adsorption of furfural through suppression of multiply

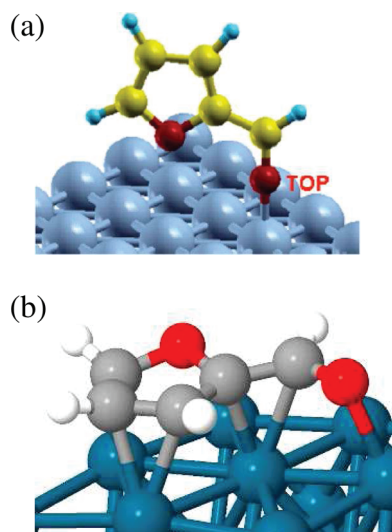


Figure 3. Optimized adsorption structures of furfural on (a) Cu(111) (reprinted with permission from ref 79. Copyright 2011 Elsevier) and (b) Pd(111) (reprinted from ref 71. Copyright 2011 American Chemical Society).

coordinated modes of adsorption. The hydrogenation of HMF over PdNi catalysts has also been recently reported.⁷⁶

Whereas there is a strong tendency for furanic compounds to adsorb in multiply coordinated structures on Pt group surfaces, on Cu and Ag surfaces much weaker adsorption is observed. Furan adsorbs on Ag(110) in a tilted configuration, desorbing by approximately 200 K during TPD experiments.⁷⁷ Similarly low TPD temperatures are observed for furan on Cu(111); in fact, unlike Pd(111), THF is more strongly adsorbed than is furan.⁷⁸ The weak interactions of furanic groups with the surface have important implications for catalysis. Resasco and co-workers⁷⁹ studied furfural hydrogenation over Cu/SiO₂ catalysts. The major product of this reaction in the temperature range 230–280 °C was found to be furfuryl alcohol, with methylfuran formed as a series reaction product at higher temperatures and residence times. The Resasco group conducted a series of kinetic experiments to fit the parameters of a Langmuir–Hinshelwood expression, and coupled this with a DFT investigation of furfural on Cu(111) and Cu(110). They found that, in contrast to similar chemistry over Pt group metal surfaces, the furan ring was actually repelled by the metal surface, with selective adsorption through the oxygenate function (Figure 3). On the basis of FTIR measurements and DFT calculations, they identified the preferred adsorption state as an η^1 aldehyde. The preference for this adsorption geometry and repulsion of the furan ring likely accounts for the high selectivity observed to alcohol products. The Resasco group also recently reported a comparative study of supported Cu, Pd, and Ni catalysts.⁸⁰ As discussed above, furfural hydrogenation primarily proceeds via decarbonylation on Pd and via formation of furfuryl alcohol on Cu. Over Ni catalysts, stronger interactions of the ring result in the appearance of ring-opened C₄ oxygenates and hydrocarbons.

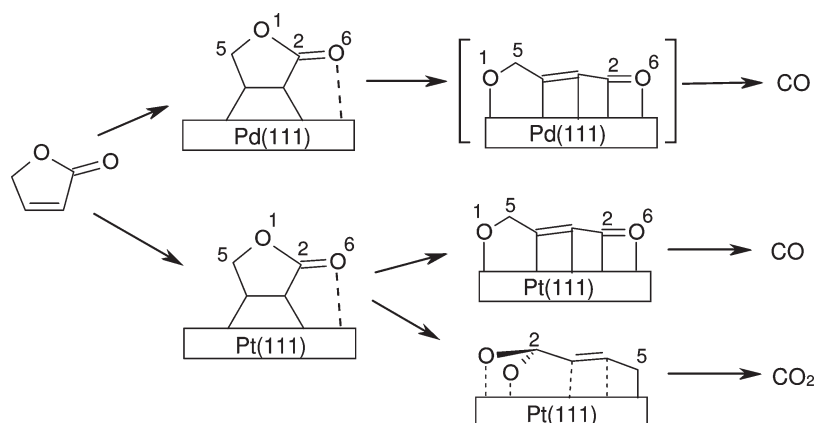
Although the main focus of this section is on hydrogenation, several groups have also begun investigating supported metal catalysts for oxidation reactions, for example, of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid, a possible renewable replacement for terephthalic acid. Significant recent research has been focused on Au nanoparticle catalysts over

various supports, though Pd and Pt catalysts have also shown activity for the reaction.^{81–83} The concentration of OH[−] species in solution plays a vital role in the reactivity, complicating efforts to understand the reaction mechanism using surface-level techniques. However, oxidation of the alcohol function of HMF proceeds through an intermediate aldehyde, likely requiring steps similar to those observed in the decomposition of furfuryl alcohol on Pd(111).⁸³ Furthermore, design of catalysts to avoid undesirable side reactions such as ring-opening or decarbonylation/decarboxylation may be able to utilize mechanistic insights for these steps over metals.⁸¹

Finally, it is worth briefly discussing similar cyclic oxygenates that are of interest for biorefining applications. Lactones such as γ -butyrolactone (GBL), γ -valerolactone (GVL), and 2(5H)-furanone (25HF) are important intermediates in various biorefining processes.^{84,85} Here, while the 5-membered ring structure is the same as for furanic compounds, the oxygen functional group is an ester rather than an ether, causing differences in reactivity related to the changed functional group and loss of symmetry of the ring. Adsorption trends at low temperature are fairly similar, however. On both Pd(111) and Pt(111), 25HF adsorbs through its olefin function, whereas the saturated lactone GBL adsorbs more weakly through its oxygenate function.^{86,87} There are two distinct positions for ring-opening on lactones (Scheme 7): C²–O¹ dissociation can lead to decarbonylation or production of dioxygenates such as diols, whereas C⁵–O¹ dissociation leads to production of surface carboxylates. On Pd(111), 25HF undergoes extensive decarbonylation on Pd(111) initiated by C²–O¹ cleavage at the carbonyl position. The two ends of the resulting adsorbate can both undergo decarbonylation, yielding two CO molecules and a C₂ fragment. However, on Pt(111) significant selectivity for C⁵–O¹ scission is observed, ultimately resulting in decarboxylation chemistry. Ring-opening processes of GBL occur with a lower activation barrier, resulting in both decarboxylation and decarbonylation.⁸⁷

Several routes involving production of fuels or chemicals from lactones have recently been proposed, with particular recent interest related to production and utilization of GVL.⁸⁸ GVL is produced from the hydrogenation/dehydration of levulinic acid, a reaction that can be carried out with high yields over Pd, Pt, and Ru catalysts, with Ru appearing to be most active.^{89,90} The reaction occurs through an Angelica lactone intermediate that, like 25HF, has a C=C bond along the ring.⁸⁹ The pathway for formation of GVL is likely to be closely related to the (reverse) reactions of 25HF and GBL that yield carboxylate intermediates, as described above. The higher yield of GVL observed over Pt-based catalysts compared to Pd appears to be consistent with the observation of enhanced carboxylate formation over Pt(111) compared to Pd(111).^{86,89} Similarly, supported metal catalysts incorporating Ru and Pd are active for the hydrogenation of succinic acid to GBL, and the subsequent ring-opening of GBL to produce 1,4-butanediol.^{91–94} Typically, a second metal such as Re is employed to increase ring-opening reactivity. Hydrogenation of GBL to 1,4-butanediol would require selective ring-opening at the bond at the C²–O¹ position; this reaction is observed to occur with high selectivity on Pd(111), consistent with the good performance of supported Pd catalysts for this reaction. More study on a variety of metal surfaces is needed to enable design of more active and selective catalysts for producing and ring-opening of lactones. However, initial indications are that efforts to design catalysts for reactions of lactones on metal surfaces based on surface science approaches may be productive.

Scheme 7. Partial Scheme for 2(5*H*)-Furanone Adsorption and Decomposition on Pd(111) and Pt(111) (Adapted from Ref 86. Copyright 2009 American Chemical Society)



In summary, the reactions of furanic compounds on metal surfaces have received far less scrutiny than reactions of α,β -unsaturated oxygenates, so that catalyst design principles are less well-developed. However, there are a few key ways in which the multifunctional nature of these molecules can control reactivity. The furan ring significantly weakens the C–O bond of pendant oxygenates, creating opportunities for new deoxygenation reactions relative to simple alcohols. Furthermore, oxygenate pendant groups can strongly affect the chemistry of the furan ring; dissociation of these groups from the furan ring produces furyl intermediates that are much more reactive on Pd(111) than furan. Finally, cyclic esters (lactones) initially adsorb in configurations similar to cyclic ethers (furans), but the asymmetry of the lactone ring creates opportunities to control ring-opening selectivity toward either carboxylates or dialkoxides based on the choice of metal.

3. REACTIONS OF POLYFUNCTIONAL MOLECULES: POLYOLS

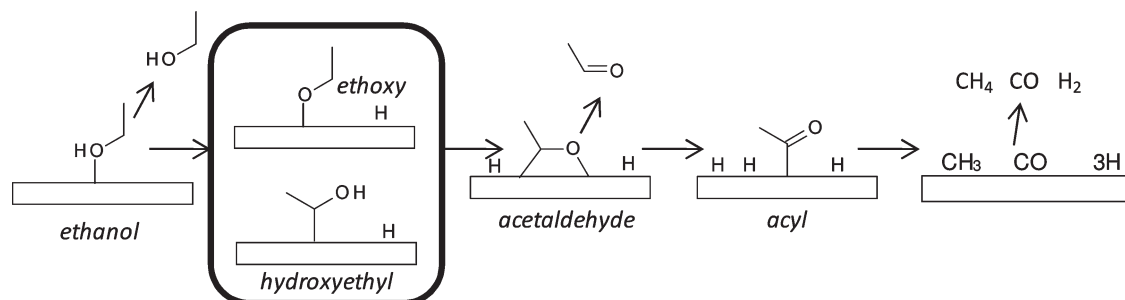
Another important class highly functional is the diols and polyols, which react on metal surfaces pathways reminiscent of those for unsaturated oxygenates. Polyols can be produced in large quantities from biomass. Glycerol is a stoichiometric byproduct of the transesterification of fatty acids to produce biodiesel.⁹⁵ Sorbitol and xylitol are produced from hydrogenation of glucose and xylose, respectively, with recent reports suggesting that alcohol sugars can be products from direct treatment of cellulose.⁹⁶ Prominent surveys of useful biorefining building blocks have included all three polyols among the top candidate chemicals, and thus they have received considerable research attention.^{97,98} Numerous transformations for polyols have been explored; for example, processes for glycerol conversion include selective oxidation to hydroxylated aldehydes and carboxylic acids, hydrogenolysis to diols, dehydration to unsaturated alcohols, dehydration to acetol and acrolein, and etherification to higher molecular weight molecules of fuels interest.^{97,99} This review will focus only on selected studies of glycerol oxidation and hydrogenolysis, with the understanding that principles of reactivity on metal surfaces may be transferrable to other technologies. The surface intermediates produced in these reactions are often comparable to those of the unsaturated oxygenates discussed above. Oxidation of polyols produces

multifunctional aldehyde intermediates, and dehydration produces unsaturated oxygenate intermediates. While differences in typical reaction conditions and the early state of fundamental studies make it difficult to make direct links between optimal catalysts, some connections are evident as indicated below.

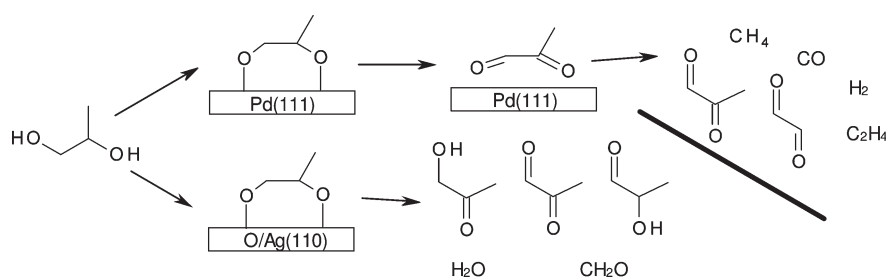
Before discussing the reactions of polyols on metal surfaces in detail, it is useful to briefly review the chemistry of monofunctional alcohols on metal surfaces. This chemistry has been investigated extensively, and only a brief overview is provided here.^{16,26,100–111} Scheme 8 shows the decomposition pathway for ethanol on Pd(111) as a representative example.¹¹² Reaction occurs through sequential dehydrogenation steps to produce an aldehyde intermediate, which undergoes decarbonylation to produce CO and adsorbed alkyls. Similar decomposition pathways are observed on Pt, Ni, and Ru surfaces.^{101,102,108,109,111,113–116} The initial decomposition step has generally been ascribed to O–H scission to produce an adsorbed alkoxide on these surfaces, though some recent studies suggest that the initial bond dissociation is a C–H scission step to produce adsorbed hydroxyalkyls.¹¹⁷ To initiate alcohol decomposition on Ag surfaces, predosed atomic oxygen is required as a Brønsted base, and on Cu either surface oxygen or elevated dosing temperature is required.^{118–120} Decomposition of alcohols has been shown to proceed through alternative or additional pathways on Rh(111),¹⁰³ where decomposition proceeds through surface oxametallacycle intermediates, and on Ag and Cu surfaces, where aldehyde decarbonylation is not observed.^{118–120} These reactivity differences suggest possible differences in selectivity for catalytic reactions of alcohols, as discussed below.

Aldehyde intermediates are prominent in the surface chemistry of alcohols, and also represent important functional groups for reactions discussed below. Aldehydes may be bound to the surface either through both their C and their O atoms in an η^2 arrangement or through the O atom via an η^1 orientation.^{14–19,121} The preference for one form over another is dictated by the composition of the surface, the presence of coadsorbates, and the molecular structure of the aldehyde. The η^1 intermediates tend to be more weakly adsorbed, whereas the more strongly adsorbed η^2 aldehydes undergo decomposition reaction including decarbonylation.

Oxidation of primary alcohols to aldehydes and carboxylic acids and of secondary alcohols to ketones has been extensively studied on supported metal catalysts such as Pt and Pd.^{122,123} The mechanism for oxidative dehydrogenation of alcohols to aldehydes and ketones is generally accepted to involve the

Scheme 8. Scheme for Ethanol Adsorption and Decomposition on Pd(111)^a

^aThe boxed intermediates represent two possible initial hydrogenation intermediates that have been proposed in the literature.

Scheme 9. Simplified Mechanism for Propylene Glycol Decomposition on Pd(111) and O-Covered Ag(110)^a

^aFor simplicity, adsorbed atomic O and OH are not shown on the Ag(110) surface. Also not shown on Ag(110) is an observed pathway in the presence of excess oxygen that results in formation and decomposition of surface formate species.

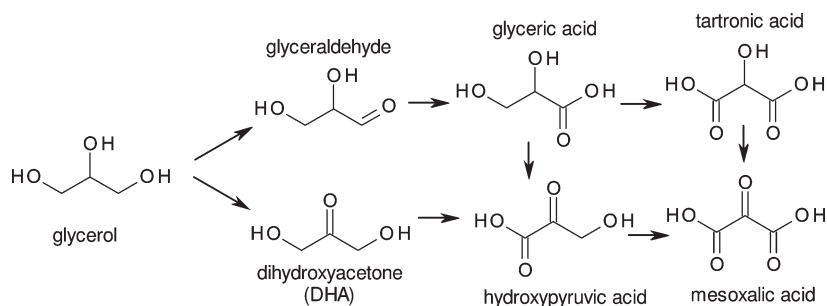
alcohol decomposition intermediates discussed above, where oxygen removes H and/or strongly adsorbed carbonaceous species from the surface through the water-forming reaction.¹²⁴ The oxidation reactions can be conducted under generally mild conditions (<100 C, <1 atm oxygen pressures), often under mildly basic pH; the use of base is particularly important for production of carboxylic acids. A variety of promoters such as Bi and Pb are generally used to improve the activity and modify the selectivity of the catalysts, but the mechanism for the promotion in general is poorly understood.¹²² Suggested roles for the promoters include the formation of favorable ensembles of active metal atoms (thus reducing the effects of self-poisoning, which is commonly observed because of the presence of strongly adsorbed intermediates),^{125,126} or stabilization of reactive OH species,¹²⁷ among other proposed explanations. As discussed below, such promoters can also be useful in the oxidation of polyols, and a better understanding of their function would be beneficial. Nanoparticle Au catalysts have also shown high activity for alcohol oxidation in basic solution.¹²⁸ Silver catalysts have been employed for alcohol oxidation, though generally in vapor-phase reaction conditions.^{129,130}

A number of surface-level studies have been conducted using diols, with relatively little work on larger polyols. We will focus in particular on the surface chemistry of ethylene glycol (EG) and 1,2-propylene glycol (PG, see Scheme 9), which have been studied on the Ag(110) and Pd(111). As with adsorbed monoalcohols on Ag surfaces, EG and PG desorb without reaction from clean Ag(110).^{131,132} When EG and PG are adsorbed on an O-covered Ag(110) surface, scission of O–H bonds and subsequent decomposition reactions are observed. Specifically, ethylene glycol decomposes to form ethylenedioxy

(–OCH₂CH₂O–) below 180 K, and this intermediate is stable up to >300 K.¹³¹ Sequential scission of C–H bonds (through a stable aldehydic alkoxide species) to produce glyoxal (CHOCHO) is observed at higher temperatures.¹³¹ Similarly, PG decomposes by 215 K on O-covered Ag(110) to produce 1,2-propanedioxy, –OCH(CH₃)CH₂O–.¹³² Propanedioxy decomposes above 300 K, but unlike EG forms a number of gas phase products including acetol (CH₃COCH₂OH), lactaldehyde (CH₃CH(OH)CHO), and pyruvaldehyde or methylglyoxal (CH₃CHOCHO). The observation of C–H scission reactions at both the primary and secondary C atoms of PG indicates that C–H scission processes are feasible at both primary and secondary C atoms. However, the earlier desorption temperature of the product acetol suggests that C–H scission at the secondary C atom is more facile.^{132,133} It is not entirely clear why partially dehydrogenated products such as acetol and lactaldehyde are observed from oxidation of PG, but similar products (particularly hydroxyacetaldehyde) are not observed from oxidation of EG.

On Pd(111), surface O is not needed for activation of O–H bonds in diols.¹³⁴ Both EG and PG decompose through proposed dialkoxide intermediates to form the adsorbed dialdehyde species glyoxal and methylglyoxal, respectively. However, in contrast to Ag(110), sequential C–H scission has not been observed; rather, evidence from vibrational spectroscopy points to the simultaneous scission of both C–H bonds. These C–H scission processes occur at higher temperature (~240 K compared to 170 K) for PG than EG, suggesting that the presence of secondary alcohol function hinders the reaction. The weaker reactivity of secondary alkoxides has also been observed in the chemistry of monofunctional alcohols on Pd(111),^{100,101} but appears to contrast with the behavior on Ag(110) as described

Scheme 10. Oxidation Pathways of Glycerol on Metal Catalysts



above. The simultaneous nature of the C–H scission processes on Pd(111) may be a result of adsorbate strain associated with sequential C–O scission, since the hydroxyl functions are on neighboring C atoms and aldehyde intermediates tend to interact strongly with Pd(111) in a flat-lying orientation. Both glyoxal and methylglyoxal desorb in small amounts above 250 K, but primarily undergo decarbonylation to produce CO, H₂, and (in the case of methylglyoxal) methane.

The surface chemistry of EG has been investigated on several other pure metals surfaces such as Rh(100), Cu(110), and Mo(110). On Rh(100), EG decomposes through ethylenedioxy by around 150 K, although at high coverage some monodentate (–OCH₂CH₂OH) species are observed that have not been reported on Ag(110) or Pd(111). Ethylenedioxy decomposes through formation of an aldehydic alkoxide intermediate (CHOCH₂O–) to ultimately form CO and H₂.¹³⁵ On Cu(110), EG decomposes through ethylenedioxy to form the dialdehyde species glyoxal, similar to the chemistry on Ag and Pd.¹³⁶ The relatively early transition metal surface Mo(110) favors carbon–oxygen bond scission, forming ethylene with 85% selectivity.¹³⁷

As discussed elsewhere in this article, using bimetallic surfaces often represents an important method for tuning selectivity in the reactions of oxygenates. To explore bimetallic effects, Chen and co-workers have investigated the chemistry of EG on Pt(111), Ni(111), and on different types of PtNi bimetallic surfaces.^{138,139} On these surfaces, EG undergoes complete decomposition to CO and H₂.¹³⁸ Decomposition is limited on the surfaces terminated by Pt but extensive on the Ni-terminated surfaces Ni(111) and Ni/Pt(111). These trends are consistent with those observed for acrolein hydrogenation discussed in Section 2; tighter binding of the C₃ oxygenate on Ni-terminated surface favors dehydrogenation over hydrogenation. The decomposition reactions again produce ethylenedioxy, which subsequently dehydrogenates all the way to CO through sequential C–H dissociation steps.^{139,140} PtFe and PtTi bimetallic surfaces have also been investigated, and it has been found that surface Fe or Ti atoms are necessary in these systems to observe substantial EG decomposition.¹⁴¹

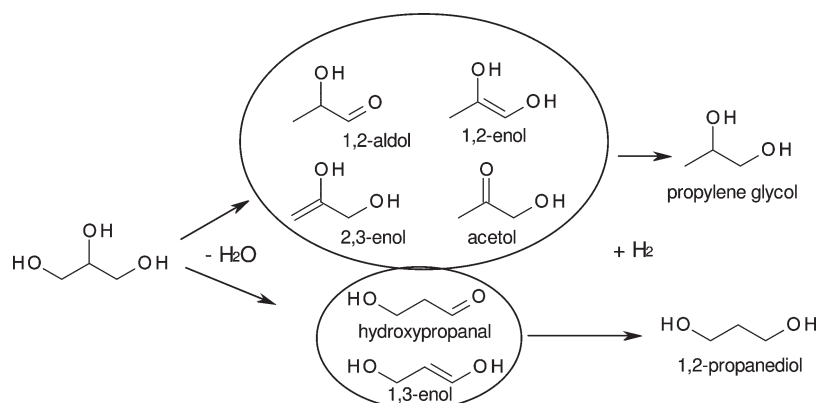
These surface studies can potentially produce insights for understanding oxidation and C–C bond-breaking reactions of polyols on supported metal catalysts. Several recent reviews discuss various aspects of these reactions.^{99,142} Most recent studies have focused on oxidation of glycerol, but there have been a few studies of diol oxidation. For example, ethylene glycol can be oxidized over Ag catalysts to form glyoxal,¹⁴³ as expected based on the surface studies described above. Over Pt catalysts, ethylene glycol can be more extensively oxidized

to produce glycolic acid.^{144,145} Propylene glycol can also be oxidized to either hydroxyacetone or hydroxypropanal and then on to further oxidation products. Interestingly, PtSn bimetallics have been found to result in high selectivities for secondary alcohol oxidation, though the mechanism for this effect is unclear.¹⁴⁶

Considerable effort has recently been devoted to investigating the selective oxidation of glycerol, which can potentially produce a number of valuable products. Scheme 10 shows the typical reaction pathways observed over metal catalysts. One reaction of interest is the selective oxidation of the interior alcohol function to produce 1,3-dihydroxyacetone (DHA). The selectivity for this reaction is generally found to be low on Pt-group catalysts and supported Au catalysts, as oxidation of the primary hydroxyl groups is facile. The generally low selectivity toward DHA appears consistent with surface science studies described above, in that primary alcohol functions are at least as reactive as secondary alcohols. Interestingly, Bi-modified Pt catalysts have been found to increase selectivity to DHA to as high as 80%, even at high conversion.^{147,148} The optimal Bi loading has been determined to be equivalent to 0.33 ML. A similar effect of modifiers such as Bi and Pb was also detected for propylene glycol oxidation, where the initial selectivity to oxidation of the secondary alcohol function was higher; interestingly, however, the modifier also promoted the further oxidation to pyruvic acid.¹⁴⁹ Bismuth often functions as a site-blocking agent on metal surfaces, and may help prevent multiple coordination of polyols on the Pt surface.¹⁴⁷ However, it is not clear why reaction of the secondary hydroxyl function would be preferred, and detailed surface-level studies of Bi-modified surfaces could shed considerable light on the mechanism. The reaction is most favored at low pH, and interactions between the acidic solution and the reaction intermediates may play a key role in producing intermediates that favor secondary alcohol oxidation.¹⁵⁰ Such a study would be useful because Bi-modified catalysts lose activity over time.¹⁵¹ The activity decrease has been attributed to blocking of the active sites by another reaction product, glyceric acid (GA).¹⁵¹ Understanding the mechanism by which Bi promotes high selectivity to DHA would be useful in designing new catalysts that could better maintain activity over time.

Over supported Pd, Pt, Rh, and Au catalysts, reaction of the primary alcohol function appears as expected to be preferred, and much research effort has focused on studying glycerol oxidation to glyceric acid.^{152–155} A similar selectivity pattern is also observed for propylene glycol oxidation over Au catalysts, with oxidation of the primary alcohol being strongly preferred.¹⁵⁶ In a recent study, Pd, Au, and Pt supported on graphite and carbon were investigated as catalysts. Au was inactive in the absence of

Scheme 11. Reaction Paths for Glycerol Hydrogenolysis to Diols (Adapted with Permission from Ref 166. Copyright 2011 RSC Publishing)



base, whereas Pd and Pt produced C₁ products. Increasing O₂ pressure improved reactivity significantly, and adding base resulted in much higher reactivities and improved selectivities toward C₃ products. For 1%Au/C, near-perfect selectivity to glyceric acid could be achieved.¹⁵⁴ For Pd and Pt, selectivities were improved, but were not as high, and activities improved as well.

Under most reaction conditions investigated to date, the oxidation of the primary alcohol function to form glyceraldehyde is rapidly followed by further oxidation to glyceric acid. In a kinetic investigation over Au catalysts, the reaction pathways to DHA and glyceric acid were found to be purely parallel; that is, selectivity between the two pathways was dictated by the position of initial oxidation and not by interconversion of DHA and glyceraldehyde.¹⁵⁷ The optimized reaction conditions for glyceric acid production are noticeably different than for DHA production, with high-pH conditions associated with the highest glyceric acid yield.¹⁵⁰ A number of investigations have focused on how catalyst supports, synthesis methods, and reaction conditions can be used to promote selectivity.^{156,158} The primary nonselective pathway proceeds through the further oxidation of glyceric acid to tartronic acid, that is, via reaction of the other primary alcohol function. Supported Au catalysts have generally been found to be more selective toward glyceric acid, with larger Au particles (having a relatively low concentration of defect sites) generally having higher stability and selectivity but reduced activity.^{152,159,160}

Bimetallic catalysts have also been investigated for glyceric acid production, particularly combinations of Pd, Pt, and Au. Improvements in selectivity and/or activity can be observed as a result of using the two metal components in tandem, showing a clear synergistic effect.^{153,161–163} In a related reaction, sorbitol oxidation, Pd, Au, and Pt by themselves have been found to be poor catalysts, but PdAu and PtAu show greatly improved activity and produce mono-oxidized products with good selectivity.¹⁶⁴ In general, the mechanism for these bimetallic effects are poorly understood, and would benefit from surface-level investigation.

The hydrogenolysis of glycerol and other alcohols is also of great interest for production of chemicals and fuels.⁶ Hydrogenolysis reactions can result in either C–C or C–O scission; for the purposes of this Perspective we will focus on the latter, which results in less oxygen-rich intermediates that are often of

greater interest for applications. Surface studies of polyol C–O hydrogenolysis have thus far been rare. This is in part because of the complexity of the reaction system: the hydrogenolysis reaction requires two steps, one an acid- or base-catalyzed dehydration and the second a metal-catalyzed hydrogenation. Many catalyst systems that show promise for efficient glycerol hydrogenolysis, such as supported Cu, have not yet been characterized extensively with surface science techniques.¹⁶⁵ Coll et al. have used DFT calculations to investigate intermediate structures for formation of propylene glycol (PG) and 1,3-propanediol (1,3-PDO) on the (111) surfaces of Ni, Pd, and Rh (Scheme 11).¹⁶⁶ They found that the metal surface can affect the initial acid–base dehydration step by stabilizing the reaction intermediates. Coll et al. tracked six dehydration pathways, with four of those leading to PG and two to 1,3-PDO. Surface-adsorbed intermediates leading to PG were in general more stable than those leading to 1,3-PDO, consistent with findings that selectivity to 1,3-PDO is generally low. However, on Rh-(111) the energy difference between 1,3-PDO-forming and PG-forming intermediates was much smaller, in line with the observation that supported Rh catalysts have the highest selectivity to 1,3-propanediol among the metals investigated.^{167,168} Finally, Pd(111) was found to stabilize intermediates more weakly than the other two surfaces, perhaps providing an explanation for its lower observed activity for the hydrogenolysis reaction.¹⁶⁹

Recent attention has been focused on the use of supported metal catalysts that have an “integrated” acid function. For example, Miyazawa et al. investigated the hydrogenolysis of glycerol to PG with an acid catalyst (Amberlyst, H₂SO₄, HCl) in concert with a metal catalyst from the group Ru, Rh, Pt, Pd. Ru with Amberlyst was the best combination. Interestingly, the Ru catalyst shows some activity for dehydration from the Ru–OH group, which leads to production of 1,3-PDO.¹⁷⁰ Dumesic and co-workers have studied glycerol hydrogenolysis on Pt, Re, and PtRe catalysts, finding that the Re component improves activity as well as selectivity toward 1,3-PDO. They proposed a direct role for the Re component, suggesting that Re–OH species could function to catalyze direct cleavage of C–OH bonds.¹⁷¹ Modification of Rh catalysts with Re, Mo, or W species has also been observed to improve activity dramatically, and improves selectivity to 1,3-PDO as well. Re appears to be the most effective among the modifiers.^{172,173} Other researchers have investigated supported Pt/WO₃ catalysts that perhaps

proceed via a similar mechanism, since both the Pt and the WO₃ must be present and be in intimate contact for the reaction to occur.¹⁷⁴

4. CONCLUSIONS AND FUTURE OUTLOOK

The widespread interest in developing catalysts for production of renewable fuels and chemicals will continue to drive research activity toward the identification of chemoselective catalysts for highly functional oxygenates. While much of the research to this point has focused on “trial-and-error” methodology to obtain a general understanding of reactivity trends, some of the examples described above show that fundamental surface science and computational investigations can potentially help guide catalyst design. Studies on model catalyst surfaces have shown close general agreement with results from catalysis for reactions such as α,β -unsaturated aldehyde hydrogenation, furfural hydrogenation, and functional alcohol oxidation, as highlighted above. Recently, such model studies have been used to successfully guide rational catalyst design for monofunctional reagents, and extension to multifunctional reagents appears possible.^{56,175–177} Because similar surface intermediates are produced in reactions such as acrolein hydrogenation and glycerol hydrogenolysis, there is the potential for insights from the studies of α,β -unsaturated aldehyde hydrogenation to be applied toward the comparably less-studied glycerol hydrogenolysis reaction.

In the design of improved catalysts for highly functional oxygenates, bimetallic and multimetallic surfaces will continue to be a major focus. As shown above, in many cases studied so far the main result of the modifying metal is to strengthen or weaken the adsorption of the oxygenate without a dramatic alteration of the preferred adsorption geometry. While such changes in binding energy can have powerful effects on catalysis, a more robust approach would be multifunctional in nature. For example, individual catalyst components would interact with a specific functional group to control the adsorption geometry of the reagent and drastically alter the potential energy landscape. Some clues toward pursuing this goal may come from bimetallics such as PtBi for glycerol oxidation, where the Bi may serve mainly as a site-blocking species to alter the adsorption geometry of glycerol. In general, developing control over the geometry of the reagent-surface complex is a key step in being able to control reactivity.

One relatively unexplored approach toward the end of controlling adsorption geometry is the use of organic surface modifiers, which in principle can interact with oxygenated reagents (e.g., through hydrophobic/hydrophilic or H-bonding interactions) to change adsorbate geometry and thus selectivity. The effectiveness of such a strategy has been convincingly demonstrated in the asymmetric hydrogenation of oxygenates such as ethyl pyruvate.¹⁷⁸ Chiral modifiers adsorbed on Pt group catalysts have been shown in many investigations to strongly promote enantioselectivity toward a specified handedness in the product molecule.¹⁷⁹ This effect appears to be due to a direct interaction between the modifier and the reagent that creates a binding geometry favorable toward production of a single enantiomer. Such ideas should be extendable to efforts to control the chemoselectivity of reactions of highly oxygenated compounds.

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