



TPD and HREELS study of the reaction of guaiacol on Zn-decorated Pt(111)

Daming Shi, John M. Vohs*

Department of Chemical & Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104-6363, USA

ARTICLE INFO

Keywords:

Guaiacol

Lignin

TPD

HREELS

Bimetallic

HDO

ABSTRACT

Temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) were used to characterize the adsorption and reaction of guaiacol on Pt(111) and Zn-modified Pt(111) surfaces. It was found that the guaiacol molecule binds to the Pt(111) surface via the aromatic ring which facilitates unselective decomposition to produce CO, H₂ and small hydrocarbon fragments at relatively low temperatures. In contrast, on Zn-modified Pt(111) surfaces, guaiacol was found to bond to surface Zn sites via the oxygen atoms in the molecule producing a bonding configuration in which the aromatic ring is tilted away from the surface. Such a binding configuration facilitates the desired C–O bond cleavage while keeping the aromatic nature of the molecule intact.

1. Introduction

Lignocellulosic biomass is attracting more and more attention as a potentially sustainable, CO₂-neutral feedstock for fuels and chemicals [1–3]. The polyaromatic nature of the lignin fraction of biomass also makes it an attractive feedstock for aromatic compounds [2,4]. Currently, the most prevalent conversion technology for lignin relies on pyrolysis [2], which produces bio-oil, biochar, and synthesis gas as products. The bio-oil is a complex mixture of phenolic compounds and lignin-derived oligomers with high oxygen content [5]. It also contains 15–30% water. The bio-oil tends to have high viscosity, high acidity, low stability, as well as low heating value. Therefore, further upgrading of the bio-oil is needed in order to form useful products. Removal of some of the oxygen via hydrodeoxygenation (HDO) is an important step in the upgrading process, although this needs to be done while maintaining the aromatic nature of the constituent molecules in order to produce high-value products.

Selective hydrogenolysis of C–O bonds is the key step in the HDO upgrading of lignin-derived biomolecules. Recently there has been a number of studies reported in the literature on the use of group 10 metals, such as Pt [6–10], Pd [9–11], and Ni [11], as catalysts for this reaction. While all of these metals are active for C–O bond hydrogenolysis, they also promote the undesirable hydrogenation of aromatic rings and tend to deactivate due to coking. Alloying these group 10 metals with a more oxyphilic metal, such as Fe [9], Sn [12], or Zn [13] has been shown to be a promising strategy for designing more selective catalysts that maintain activity for C–O bond hydrogenolysis while simultaneously having low activity for ring hydrogenation. Insight into

the mechanism by which alloying with a more oxyphilic metal affects activity and selectivity, however, is only starting to emerge.

In previous studies we have investigated the adsorption and reaction of aromatic oxygenates that contain aldehyde (benzaldehyde) [14] and alkoxide (anisole) [13] functionalities on model catalysts consisting of Pt(111) and Zn-decorated Pt(111) surfaces. These studies show that Zn addition to Pt alters the d-band of the metal in such a way that it decreases the binding of the aromatic group to the surface. These studies along with those for simpler oxygenates, such as methanol and acetaldehyde [15,16], also indicate that the Zn atoms provide bonding sites for the oxygen atoms in these molecules and that this may help facilitate selective cleavage of C–O bonds.

In the work described here we have expanded our previous investigations of the adsorption and reaction of lignin-derived model compounds on model catalysts consisting of Pt(111) and Zn-decorated Pt(111) surfaces [13,14] to include guaiacol which contains both alkoxide and hydroxyl functionalities. Temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) were used to investigate reaction pathways and determine the bonding configurations of stable adsorbed intermediates formed from guaiacol. This study in conjunction with our previous work provide considerable new insight into how alloying a group 10 metal with a more oxyphilic metal, such as Zn, affects the reaction pathways, adsorbed intermediates, and active sites for C–O bond cleavage in aromatic oxygenates such as those found in pyrolysis oils produced from lignin.

* Corresponding author.

E-mail address: vohs@seas.upenn.edu (J.M. Vohs).

<http://dx.doi.org/10.1016/j.cattod.2017.07.002>

Received 8 December 2016; Received in revised form 24 May 2017; Accepted 3 July 2017
0920-5861/ © 2017 Elsevier B.V. All rights reserved.

2. Experimental

Both TPD and HREELS experiments were conducted in a UHV apparatus described in detail in previous publications [16–18]. The system was equipped with a quadrupole mass spectrometer (SRS RG-A200), an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies) and had a background pressure of 2×10^{-10} Torr. A Pt(111) single crystal substrate which was 10 mm in diameter and oriented to within $\pm 0.5^\circ$ was spot-welded to two tantalum wires that were connected to the UHV sample manipulator. The Pt(111) surface was cleaned by repeated cycles of 2 kV Ar^+ ion bombardment at 600 K for 40 min, annealing at 1200 K under 2×10^{-8} Torr O_2 for 15 min, and annealing at 1200 K in vacuum for 5 min. The sample was heated resistively and cooled to 110 K by conduction from a liquid N_2 reservoir.

Zn deposition on Pt(111) was obtained by exposing the Pt surface to a beam of Zn atoms produced from a thermal evaporative source consisting of a coil of Zn wire (Alfa Aesa, 99.99%) around a resistively-heated tungsten filament. The Zn flux from this source was monitored using a quartz crystal microbalance (QCM) that was located midway between the source and the sample but positioned below the sample in order to not block the flux of atoms to the Pt crystal. One monolayer of Zn was assumed to have the same density of atoms as that on the Pt (111) surface, i.e., 1.51×10^{15} atoms/ cm^2 .

In a previous study [19] it was shown that Zn atoms vapor deposited on Pt(111) remain on the surface at temperatures below 600 K, while at higher temperatures they diffuse into the surface where they form a substitutional alloy in which the Zn primarily resides in the second layer [19]. Since the goal of the present study was to assess how addition of Zn to Pt influences reactivity, both through electronic effects and by providing specific sites for adsorption, we chose to use a Pt(111) surface decorated with Zn adatoms as a model PtZn alloy surface.

The guaiacol reactant (Sigma Aldrich, 99.8%) was contained in a glass vial attached to a stainless steel manifold that was connected to the main UHV apparatus via a variable leak valve that was equipped on the UHV side with a directional dosing tube. While dosing guaiacol the sample was positioned directly in front of the dosing tube allowing a lower base pressure to be maintained for vacuum chamber. Based on previous calibration studies the dosing tube enhanced the reactant gas pressure at the sample surface by a factor of 10-fold relative to that measured in the vacuum chamber.

TPD experiments as a function of the guaiacol dose were performed for the Pt(111) surface in order to determine the dosage that resulted in saturation of the low-temperature guaiacol peak from the Pt(111) surface which corresponds to the desorption of second layer guaiacol. Based on these experiments it was determined that saturation of the surface with guaiacol occurred for a 0.5 L (1 L = 10^{-6} Torr) dose and this dosage was used in all subsequent TPD and HREEL experiments. Note that this dose ensured that all the experiments in this study were done using surfaces that were completely saturated with chemisorbed guaiacol. A heating rate of 3 K/s was used in the TPD experiments and the HREEL spectra were collected using a 4 eV electron beam oriented at 60° with respect to the surface normal. The full width at half-maximum of the elastic peak obtained from the clean surface was typically 40 cm^{-1} . HREEL spectra were collected as a function of sample temperature. For temperatures greater than the dosing temperature the sample was heated at 3 K/s to the indicated temperature and then rapidly quenched to low temperature at which point the spectrum was collected.

3. Results and discussion

3.1. TPD of guaiacol on Pt(111) and Zn/Pt(111) surfaces

TPD results for Pt(111) dosed with 0.5 L of guaiacol are displayed in Fig. 1. In addition to a narrow guaiacol peak at 225 K, which based on

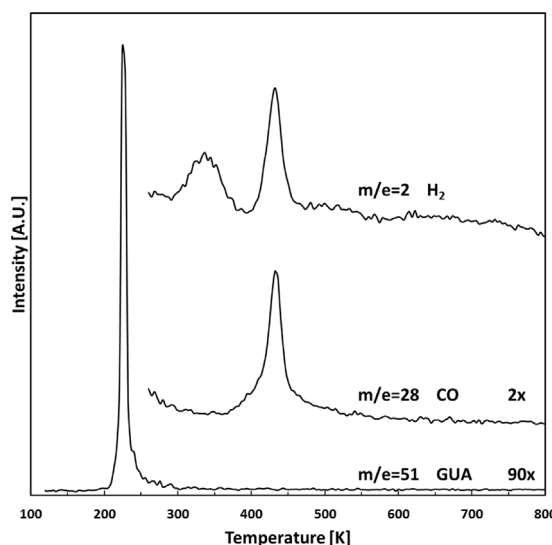


Fig. 1. TPD spectra obtained following exposure of the Pt(111) surface to 0.5 L of guaiacol (GUA).

previous studies of similar aromatic molecules on Pt(111) can be assigned to desorption of second layer physisorbed species [20], the only other desorbing species were H_2 at 340 and 435 K, and CO at 435 K. The fact that the CO and H_2 peaks at 435 K occur at the same temperature and have similar shapes suggests that they are reaction-limited products of the decomposition of a common adsorbed intermediate. Since CO was the only carbon-containing reaction product this decomposition reaction must also result in carbon deposition on the surface. Assuming that all of the oxygen in the guaiacol reactant is accounted for in the CO product along with the 7:2 carbon-to-oxygen ratio in the guaiacol reactant, the TPD data indicate that roughly 2.5 carbon atoms were deposited on the surface for every CO molecule produced. The lower-temperature H_2 peak at 340 K is consistent with a desorption-limited process [21] and thus demonstrates that dehydrogenation of at least a portion of the adsorbed guaiacol must occur below this temperature.

For TPD studies of the reactivity of Zn modified Pt(111) surfaces a 0.4 ML Zn/Pt(111) surface was chosen as a representative model alloy surface. Consistent with our previous studies [14,22], addition of Zn adatoms to the Pt(111) surface caused a significant change in reactivity. Fig. 2 displays TPD data for a 0.4 ML Zn/Pt(111) surface dosed with

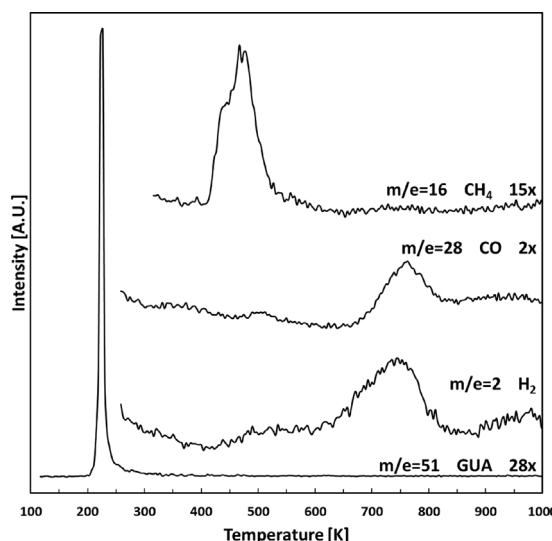


Fig. 2. TPD spectra obtained following exposure of the Zn/Pt(111) surface to 0.5 L of guaiacol (GUA) (These data are displayed on the same scale as those in Fig. 1.).

0.5 L of guaiacol. For this surface a narrow guaiacol peak at 225 K corresponding to physisorbed species is again observed. Other notable features are CO and H₂ peaks at 750 K indicating the decomposition of an adsorbed intermediate occurs at this temperature. Note that this is over 300 K higher than the corresponding peaks for the Zn-free surface demonstrating that Zn addition results in significant stabilization of the adsorbed species. Additional features in the TPD data include a smaller H₂ peak centered at 525 K and a small CH₄ desorption peak at 480 K. This latter peak indicates that scission of the C–O bond in the –O–CH₃ group in at least some of the adsorbed guaiacol occurs at or below this temperature. As was the case for Pt(111) these data also indicate that carbon is deposited on the surface after a guaiacol TPD run. Quantification of the TPD data indicates that roughly 2.25 carbon atoms were deposited on the surface for every CO molecule produced (this again assumes all of the oxygen in the guaiacol reactant is accounted for in the CO product). The quantification of the TPD data also reveals that the saturation coverage of chemisorbed guaiacol on the Pt(111) was approximately 10% higher than that on and Zn/Pt(111). It is also noteworthy that Pt(111) surfaces covered with multilayers of Zn were found to be unreactive towards guaiacol, thus demonstrating that the chemistry observed for the 0.4 ML Zn/Pt(111) surface cannot be attributed completely to reaction on surface Zn sites.

3.2. HREELS of guaiacol on Pt(111) and Zn/Pt(111) surfaces

HREEL spectroscopy was used to identify the stable surface intermediates and their reaction and interconversion as a function of surface temperature. HREEL spectra collected as a function of temperature for Zn-free and 0.4 ML Zn–Pt(111) surfaces with a 0.5 guaiacol dosage at 120 K are displayed in Figs. 3 and 4, respectively. For both the Zn-free and Zn-modified Pt(111) surfaces, the spectra at 150 K contain characteristic peaks of molecular guaiacol which can be assigned by

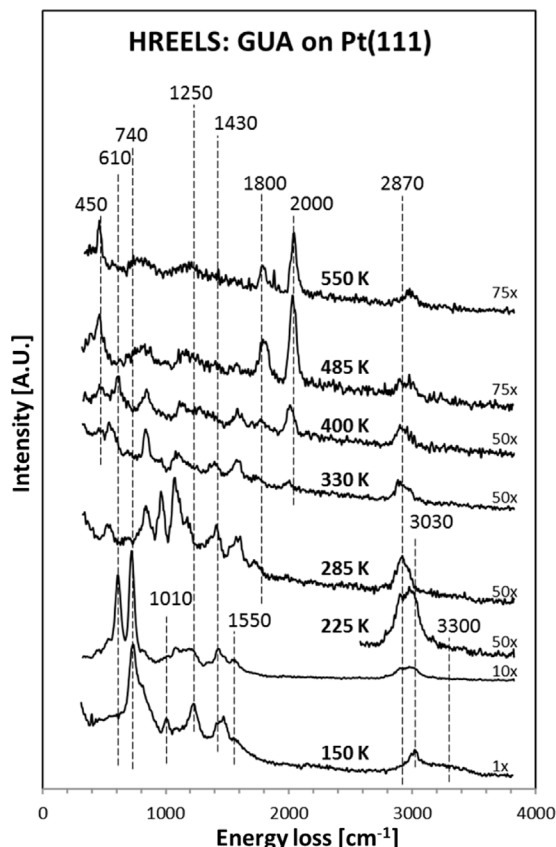


Fig. 3. HREEL spectra as a function of temperature for Pt(111) dosed with 0.5 L guaiacol at 115 K.

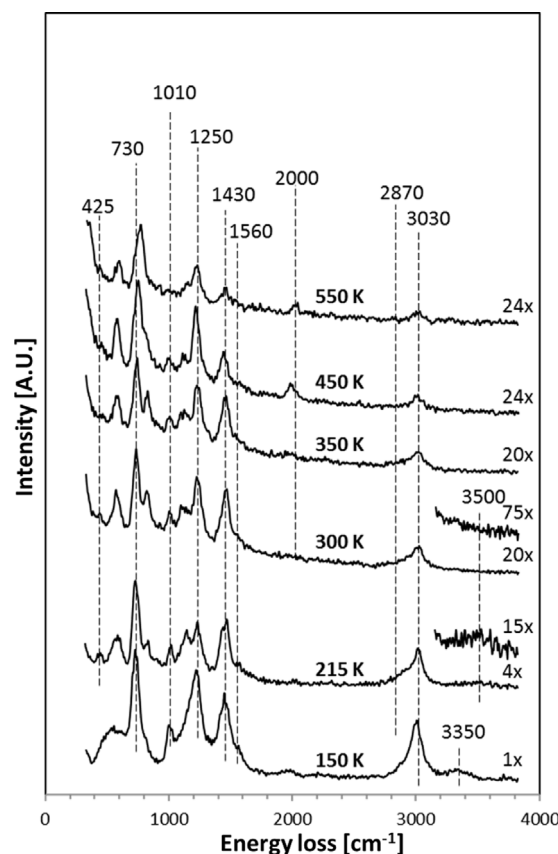


Fig. 4. HREEL spectra as a function of temperature for Zn/Pt(111) dosed with 0.5 L guaiacol at 115 K.

Table 1
Vibrational mode assignment.

mode	frequency cm ⁻¹		
	IR/Raman [23,24]	Pt(111)	Zn/Pt(111)
Ring deformation (out-of-plane)	584,583	580	580
b (CCO) (out-of-plane)	741,727	740	730
γ (C–H) _{ring} (out of plane mode)	823,859	830	840
b (CCH) (in-plane mode) + ν (O–Me)	1024,1027,1040	1010	1080
b (OCH) + b (CCH) _{ring} (in-plane mode)	1156,1157,1111,73,1172	–	1150
ν (C–OMe) + ν (C–OH)	1225,1261	1250	1250
b (HCH)	1444,1443,1458,1454	1430	1430
ν (C–C) _{ring} (in plane mode)	1502,1597	1550	1560
ν (C–H) _{methyl}	2840,2950,2965	2870	2870
ν (C–H) _{ring}	3052	3030	3030
ν(O–H)	–	–	3500
ν(O–H) (hydrogen bonded)	3330	3300	3350
ν (Pt–O)	–	505	–
ν (Zn–O)	–	–	425
ν (Pt–C)	–	450	–

s – symmetric, as – asymmetric, b – bend, ν – stretch, δ – deformation, ρ – rock, γ – wag, χ – scissor.

comparison to the corresponding IR and Raman spectra [23,24] of the free molecule. These peak assignments are presented in Table 1. Note that the characteristic peaks for guaiacol include the b(CCO) at 740 cm⁻¹, ν(C–O) at 1250 cm⁻¹, ν(C–H)_{methyl} at 2870 cm⁻¹, ν(C–H)_{ring} at 3030 cm⁻¹ and a hydrogen bonded ν(O–H) peak at 3300 cm⁻¹.

As shown in Fig. 3, heating the guaiacol-dosed Pt(111) surface to 225 K caused several changes in the HREEL spectrum of the adsorbed

species. Since heating to this temperature is sufficient to desorb any weakly-bound guaiacol (see Fig. 1), this spectrum corresponds to chemisorbed species. One subtle change that occurred upon heating is a small decrease in the intensities of the peaks for the in-plane modes between 900 and 1600 cm^{-1} relative to that of the prominent CCO out-of-plane bending peak at 740 cm^{-1} . In our previous studies of the adsorption of benzaldehyde and anisole on Pt(111) [13,14], similar changes in the HREEL spectra that occurred upon heating to desorb weakly-bound species could be attributed to a bonding configuration of the chemisorbed molecule in which the aromatic ring is situated parallel to the surface. Due to induced image dipoles in the metal, this configuration causes a decrease in the intensities of the in-plane vibrational modes. While an analysis of the changes in the relative intensities of the vibrational peaks for adsorbed guaiacol is less clear on this point, previous DFT studies indicate that a binding configuration in which the aromatic ring in guaiacol is parallel to the Pt(111) surface is also the most energetically favorable [25,26]. Other more prominent changes in the spectrum upon heating to 225 K include the emergence of an intense peak at 610 cm^{-1} and the disappearance of the broad $\nu(\text{O}-\text{H})$ peak between 3200 and 3600 cm^{-1} . This latter peak was broad in the 150 K spectrum due to hydrogen bonding in the physisorbed multilayer and it is notable that it was not replaced by a distinct $\nu(\text{O}-\text{H})$ peak in the OH stretching region of the spectrum. A change in the relative intensities of the aromatic and aliphatic $\nu(\text{C}-\text{H})$ peaks at 3030 cm^{-1} and 2870 cm^{-1} , respectively, is also apparent, with that of the aliphatic peak increasing relative to that of the aromatic peak.

Together all of these changes indicate that the guaiacol has undergone some reaction upon heating to 225 K. Unfortunately based on the HREEL spectrum alone it is not possible to definitively determine the structure of the adsorbed intermediate(s) at this temperature. The intense peak at 610 cm^{-1} is particularly difficult to assign, although a $\delta(\text{CCO})$ mode is one possibility [16]. It is noteworthy, however, that in previous studies of the reactions of phenol and anisole on Pt(111) [13,20], cyclohexadienone was identified as an adsorbed intermediate and this species exhibited an HREEL spectrum that shares features similar to that observed here for guaiacol-dosed Pt(111) at 225 K. Thus, it is likely that the guaiacol reacts on Pt(111) to form the analogous 2-methoxy-2,5-cyclohexadien-1-one. The structure of this species is shown in Fig. 5, as well as a possible surface bonding configuration in which the ring is parallel to the surface.

Heating the surface to 285 K caused several more prominent changes in the spectrum of the adsorbed species including the disappearance of the intense peaks at 610 and 740 cm^{-1} , the emergence of a series of new peaks between 800 and 1200 cm^{-1} , and the disappearance of the $\nu(\text{CH})_{\text{ring}}$ peak at 3030 cm^{-1} as well as the ring out-of-plane $\delta(\text{CCO})$ peak at 740 cm^{-1} . These latter two changes indicate the loss of the aromatic character of the adsorbed species. While we are

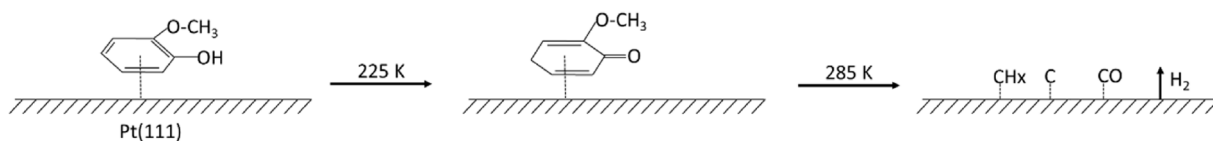
not able to definitively assign this spectrum to a specific adsorbed intermediate(s), these changes clearly show that significant decomposition of the adsorbed guaiacol has occurred by this temperature. This is consistent with the TPD results which show H_2 desorption commencing at 280 K.

Spectra obtained after heating to higher temperatures provides additional evidence for unselective decomposition of the adsorbed guaiacol on Pt(111). At 485 K the spectrum is dominated by peaks at 1800 and 2000 cm^{-1} corresponding to the $\nu(\text{C}-\text{O})$ modes of CO adsorbed in bridge and atop sites, respectively. The C-H stretch at 2870 cm^{-1} , the series of small peaks between 600 and 1500 cm^{-1} , and the emergence of a peak at 450 cm^{-1} , which can be assigned to C-Pt stretch, all indicate that some hydrocarbon fragments are also present on this surface at this temperature.

HREELS data as a function of temperature for a guaiacol on a Zn-modified Pt(111) surface are displayed in Fig. 4. A 0.4 ML Zn coverage was selected here as a representative Zn adatom surface. The spectra were again obtained after saturating the surface with 0.5 L guaiacol at 150 K and then briefly heating to the indicated temperatures. As noted above, at 150 K the spectrum is similar to that obtained for this temperature from the Zn-free Pt(111) and is consistent with the IR and Raman spectrum of molecular guaiacol (see Table 1) [23,24]. Heating to 215 K to desorb the weakly bound physisorbed guaiacol produced relatively few changes in the spectrum. Indeed, the spectrum of the adsorbed species is remarkably similar for annealing temperatures between 215 and 450 K, although some subtle differences are observed. It is particularly noteworthy that the $\nu(\text{C}-\text{H})_{\text{ring}}$ peak at 3030 cm^{-1} remained unchanged up to 450 K, demonstrating that the aromatic ring remains intact up to this temperature. This is in stark contrast to what was observed for the Zn-free Pt(111) surface where complete loss of the aromatic character of the adsorbed species occurred by 285 K.

One change that is apparent upon heating from 215 to 300 K is the disappearance of the O-H stretching peak at 3500 cm^{-1} . A small but distinct peak also emerges at 425 cm^{-1} in this temperature range. Based on our previous studies of Zn-modified surfaces [13,15] we assign this latter feature to a $\nu(\text{Zn}-\text{O})$ stretching mode. Meanwhile, some minor changes in the relative intensities of the ring in-plane and out-of-plane vibrational modes were also observed upon heating to 300 K; however, unlike the case of Zn-free Pt(111), no significant diminution of the in-plane modes was observed, indicating that the aromatic ring is tilted away from the Zn-modified surface. Previous studies of the adsorption of other aromatic oxygenates on Pt(111) surfaces, such as benzaldehyde and anisole, have also reported that Zn addition to the surface results in bonding configurations in which the aromatic ring is tilted away from the surface [13,14]. Together these changes indicate that the O-H group in guaiacol undergoes dissociation on Zn/Pt(111) at temperatures below 300 K with bonding of the hydroxyl oxygen most

Guaiacol on Pt(111) surface



Guaiacol on Zn/Pt(111) surface

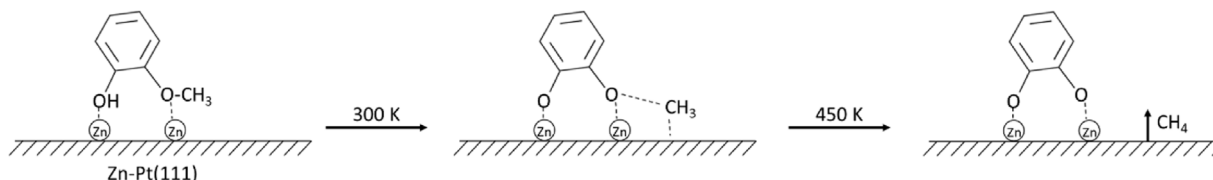


Fig. 5. Proposed pathways and intermediates for the adsorption and reaction of guaiacol on Pt(111) and Zn/Pt(111) surfaces.

likely occurring at a Zn site as shown schematically in Fig. 5. The conclusion that the oxygen binds to Zn sites is also consistent with previous studies in which it was shown by XPS that methanol adsorbs via the oxygen on Zn sites on Zn/Pt(111) [15].

Additional changes observed in the HREEL spectra upon heating the guaiacol-dosed Zn/Pt(111) surface to 450 K and above, include the disappearance of the $\nu(\text{C}-\text{H})_{\text{methyl}}$ peak at 2870 cm^{-1} as well as the emergence of a small peak at 2000 cm^{-1} , which is indicative of the $\nu(\text{C}-\text{O})$ mode of adsorbed atop CO species. It is possible that this latter peak is due to adsorption of some CO from the chamber background. A gradual decrease in the intensity of the peak at 1010 cm^{-1} , which is due primarily to the $\nu(\text{O}-\text{Me})$ stretch, is also observed upon heating to 450 K. We propose that this results from cleavage of the O-Me bond in at least a portion of the adsorbed species. This scenario is consistent with the TPD results which show the production of CH_4 as a primary product starting at 400 K. It is likely that this C–O bond dissociation reaction also involves an oxyphilic Zn site (see Fig. 5), although we have no direct evidence for this.

Fig. 5 shows a schematic of a proposed reaction pathway for guaiacol on Zn/Pt(111) that is consistent with our TPD and HREELS data. The added Zn alters the electronic properties of the surface that causes a decrease in its interaction with the aromatic ring and guaiacol interacts with Zn/Pt(111) primarily through the O atoms with dissociation of the O–H group occurring below 300 K at a Zn site. This is followed by O– CH_3 bond cleavage which occurs between 300 and 450 K. A proposed transition state for this reaction is shown in Fig. 5 in which the methoxide O bonds to a Zn site and the methyl carbon bonds to an adjacent Pt site. This reaction produces a catechol-like intermediate bonded via the oxygens to Zn sites. This conclusion is consistent with previous studies that have reported catechol as one of the products produced during the HDO of guaiacol over bimetallic catalyst such as Pd–Fe [9] and Pt–Sn [12]. This intermediate is stable on the surface to temperatures in excess of 550 K. A similar pathway and active sites has been reported for O– CH_3 bond cleavage in adsorbed anisole on Zn/Pt(111) [13].

The HREELS results together with the TPD data vividly demonstrate that Zn addition results in significant stabilization of adsorbed guaiacol on the Pt(111) surface. This is consistent with previous studies of the reaction of aldehydes and biomass-derived oxygenates on Zn-modified Pt surfaces where it has been shown that Zn addition decreases the activity of the Pt(111) surface for both C–C and C–H bond cleavage [13,14,16,22], while simultaneously facilitating C–O bond cleavage. While not investigated here, the weakening of the interaction of the aromatic ring with the Pt(111) surface upon Zn addition resulting in the ring tilting away from the surface would also likely decrease the propensity of the ring to become hydrogenated under typical hydrodeoxygenation reaction conditions. Since ring hydrogenation is usually undesirable this could be another positive attribute of PtZn catalysts.

4. Conclusions

This study provides useful insight into the adsorption and reaction of the lignin-derived oxygenate, guaiacol, on Pt(111) and Zn-modified Pt(111) surfaces. For Zn-free Pt(111), guaiacol interacts with the surface via the π -orbitals of the aromatic ring with the ring situated parallel to the surface. Such binding configuration promoted unselective decomposition with loss of the aromatic character of the ring occurring at temperatures as low as 225 K. Modifying the Pt(111) surface with Zn adatoms, however, was found to significantly alter the binding configuration of guaiacol. On this surface the aromatic ring interacted less strongly with the surface and the guaiacol molecule underwent dissociative adsorption at the hydroxyl group with bonding to the surface occurring primarily via this oxygen at a Zn site with the aromatic ring

tilted away from the surface. Such a binding configuration facilitated O– CH_3 bond cleavage and would likely limit hydrogenation of the ring under typical HDO reaction conditions.

Acknowledgment

Funding for this study was provided by the National Science Foundation grant no. CBET-1508048.

References

- [1] H. Wang, J. Male, Y. Wang, Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds, *ACS Catal.* 3 (2013) 1047–1070.
- [2] J. Zakzeski, P.C. Bruijninx, A.L. Jongerius, B.M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, *Chem. Rev.* 110 (2010) 3552–3599.
- [3] G.W. Huber, J.A. Dumesic, An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery, *Catal. Today* 111 (2006) 119–132.
- [4] E. Adler, Lignin chemistry—past, present and future, *Wood Sci. Technol.* 11 (1977) 169–218.
- [5] T. Sfetsas, C. Michailof, A. Lappas, Q. Li, B. Kneale, Qualitative and quantitative analysis of pyrolysis oil by gas chromatography with flame ionization detection and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry, *J. Chromatogr. A* 1218 (2011) 3317–3325.
- [6] A. Gutierrez, R. Kaila, M. Honkela, R. Slioor, A. Krause, Hydrodeoxygenation of guaiacol on noble metal catalysts, *Catal. Today* 147 (2009) 239–246.
- [7] D. Gao, C. Schweitzer, H.T. Hwang, A. Varma, Conversion of guaiacol on noble metal catalysts: reaction performance and deactivation studies, *Ind. Eng. Chem. Res.* 53 (2014) 18658–18667.
- [8] T. Nimmanwudipong, C. Aydin, J. Lu, R.C. Runnebaum, K.C. Brodwater, N.D. Browning, D.E. Block, B.C. Gates, Selective hydrodeoxygenation of guaiacol catalyzed by platinum supported on magnesium oxide, *Catal. Lett.* 142 (2012) 1190–1196.
- [9] J. Sun, A.M. Karim, H. Zhang, L. Kovarik, X.S. Li, A.J. Hensley, J.-S. McEwen, Y. Wang, Carbon-supported bimetallic Pd–Fe catalysts for vapor-phase hydrodeoxygenation of guaiacol, *J. Catal.* 306 (2013) 47–57.
- [10] C. Zhao, J. He, A.A. Lemonidou, X. Li, J.A. Lercher, Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes, *J. Catal.* 280 (2011) 8–16.
- [11] J. Chang, T. Danuthai, S. Dewiyanthi, C. Wang, A. Borgna, Hydrodeoxygenation of guaiacol over carbon-supported metal catalysts, *ChemCatChem* 5 (2013) 3041–3049.
- [12] M. Á. González-Borja, D.E. Resasco, Anisole and guaiacol hydrodeoxygenation over monolithic Pt–Sn catalysts, *Energy Fuels* 25 (2011) 4155–4162.
- [13] D. Shi, L. Arroyo-Ramirez, J.M. Vohs, The use of bimetallics to control the selectivity for the upgrading of lignin-derived oxygenates: reaction of anisole on Pt and PtZn catalysts, *J. Catal.* 340 (2016) 219–226.
- [14] D. Shi, J.M. Vohs, Lignin-derived oxygenate reforming on a bimetallic surface: the reaction of benzaldehyde on Zn/Pt 111, *Surf. Sci.* (2015).
- [15] E. Martono, J.M. Vohs, Reaction of CO, CH_2O CH_3OH on Zn-modified Pt (111) surfaces, *J. Phys. Chem. C* 117 (2013) 6692–6701.
- [16] J.R. McManus, E. Martono, J.M. Vohs, Selective deoxygenation of aldehydes: the reaction of acetaldehyde and glycolaldehyde on Zn/Pt (111) bimetallic surfaces, *ACS Catal.* 3 (2013) 1739–1750.
- [17] J.R. McManus, M. Saliccioli, W. Yu, D.G. Vlachos, J.G. Chen, J.M. Vohs, Correlating the surface chemistry of C2 and C3 aldehydes with a C6 sugar: reaction of glucose, glyceraldehyde, and glycolaldehyde on Pd (111), *J. Phys. Chem. C* 116 (2012) 18891–18898.
- [18] J.R. McManus, J.M. Vohs, Deoxygenation of glycolaldehyde and furfural on $\text{Mo}_2\text{C}/\text{Mo}$ 100, *Surf. Sci.* (2014).
- [19] C.-S. Ho, E. Martono, S. Banerjee, J. Roszell, J. Vohs, B.E. Koel, Alloy formation and chemisorption at Zn/Pt (111) bimetallic surfaces using alkali ISS, XPD, and TPD, *J. Phys. Chem. A* 117 (2013) 11684–11694.
- [20] H. Ihm, J. White, Stepwise dissociation of thermally activated phenol on Pt (111), *J. Phys. Chem. B* 104 (2000) 6202–6211.
- [21] K. Christmann, G. Ertl, T. Pignet, Adsorption of hydrogen on a Pt (111) surface, *Surf. Sci.* 54 (1976) 365–392.
- [22] D. Shi, J.M. Vohs, Deoxygenation of biomass-derived oxygenates: reaction of furfural on Zn-modified Pt (111), *ACS Catal.* 5 (2015) 2177–2183.
- [23] L.N.a.T. Tripathi, *Proc. Int. Conf. Spectry, Bombay*, 1967.
- [24] V. Verma, K. Nair, D. Rai, Vibrational spectra and thermodynamic functions of the three isomeric methoxyphenols, *Isr. J. Chem.* 8 (1970) 777–789.
- [25] K. Lee, G.H. Gu, C.A. Mullen, A.A. Boateng, D.G. Vlachos, Guaiacol hydrodeoxygenation mechanism on Pt (111): insights from density functional theory and linear free energy relations, *ChemSusChem* 8 (2015) 315–322.
- [26] J. Lu, S. Behtash, O. Mamun, A. Heyden, Theoretical investigation of the reaction mechanism of the guaiacol hydrogenation over a Pt (111) catalyst, *ACS Catal.* 5 (2015) 2423–2435.