Mechanistic study of the hydrodeoxygenation of lignin-derived oxygenates on a CoPt bimetallic catalyst: reaction of anisole on Co-modified Pt(111)

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Abstract
Temperature programmed desorption and high-resolution electron energy loss spectroscopy were used to characterize the adsorption and reaction of anisole (C₆H₅–OCH₃) on Pt(111) and Co-decorated Pt(111) surfaces. On both surfaces anisole was found to undergo O–CH₃ bond cleavage to form an oxocyclohexadienyl-structured intermediate (C₆H₆O) which bonds to the surface in a η₅-π configuration. Interaction of the O atom in this intermediate with Co adatoms was found to facilitate selective cleavage of the C–O bond to produce adsorbed benzene or phenyl groups. In parallel with this pathway, unselective decomposition of adsorbed anisole was also found to occur. The results obtained in this study along with those previously reported for the reaction of anisole on Zn-decorated Pt(111) surfaces provide further insight into how the addition of a second more oxyphilic metal to Pt affects surface reaction pathways and the hydrodeoxygenation selectivity of lignin-derived aromatic oxygenates.

Introduction
There has been a growing interest in the development of technologies that use renewable resources, such as lignocellulosic biomass, as an alternative to fossil-based resources as feedstocks for the production of a range of fuels and chemicals [1–3]. While much effort has focused on methods for upgrading the cellulose and hemicellulose fractions of biomass, especially for the production of hydrocarbon-based fuels [4, 5], until recently utilization of the lignose fraction has received much less attention. While the highly branched, polyphenolic nature of lignin makes it more refractory and, therefore, more difficult to process compared to cellulose, these same properties make it an attractive feedstock for a range of high-value aromatic compounds [6, 7]. The constituent, substituted aromatic molecules that are produced by lignin depolymerization via pyrolysis or other means also generally require additional processing. In particular, the presence of oxygenated substituents on the aromatic rings make hydrodeoxygenation (HDO) an important step in the overall upgrading process [5, 6].

While supported group 10 metals (i.e. Ni, Pd, Pt) are known to be active HDO catalysts, they also have high activity for the hydrogenation of aromatic rings leading to less-desirable saturated ring products when used for the HDO of lignin-derived aromatic oxygenates [8–11]. Alloying a group 10 metal with a second oxyphilic metal such as Fe or Zn [12–15] has emerged as a promising approach to overcome this problem and such catalysts show higher HDO selectivity to the desired aromatic products. In order to understand the mechanism by which the addition of the oxyphilic metal affects the overall catalyst HDO activity and selectivity our group has undertaken a series of mechanistic studies of the reaction of lignin-derived aromatic oxygenates, including benzaldehyde, anisole, and guaiacol, on ZnPt model catalysts consisting of a Pt(111) surface decorated with Zn adatoms [16–18]. These studies have revealed that the Zn additive has multiple effects including providing a binding site for the oxygen atoms in the reactant molecules which helps facilitate selective C–O bond cleavage. The Zn also has a longer range electronic effect that destabilizes the bonding of phenyl rings to the Pt surface.
This destabilization is sufficient to change the bonding configuration of phenyl compounds on Pt(111) from one where the ring lays flat on the surface to one where it is tilted away from the surface. We have argued that this change in bonding configuration is responsible for the decrease in the ring hydrogenation activity of ZnPt compared to Pt alone.

While our previous studies have provided considerable insight into how Zn alters the HDO activity of Pt, it is not clear how general these observations are and if the addition of other oxyphilic metals to Pt will have a similar effect. Cobalt is another oxyphilic metal that has been used to modify the HDO activity of Pt. Previous studies [19–22], however, provide a somewhat contradictory picture of the effect of Co addition. For example, in experimental and theoretical studies of the HDO of both furfural and 5-hydroxymethylfurfural over carbon-supported PtCo nanocrystals, Gorte and co-workers reported that a surface cobalt oxide layer weakens the interaction of the furan ring with the surface which helps prevent over-hydrogenation and ring opening [19, 20], an effect that is similar to what we have observed for Zn. In contrast, Do et al have studied the HDO of m-cresol over alumina-supported Pt and PtCo catalysts and reported that the addition of Co increases the overall HDO activity and the rate of formation of the saturated ring product, methylcyclohexane [22]. These previous studies have motivated us to expand our studies of oxyphilic metal modifiers on the HDO activity of Pt to include Co. In particular, in the work reported here we have investigated the adsorption and reaction of anisole on Pt(111) surfaces modified with Co adatoms with the goal of elucidating how the Co modifier affects the interaction of the aromatic ring with the surface and the overall reaction pathways.

**Experimental**

In this study temperature programmed desorption (TPD) was used to assess surface reaction pathways and high resolution electron energy loss spectroscopy (HREELS) was used to identify adsorbed reaction intermediates and their bonding configurations. These experiments were conducting using an ultra-high vacuum (UHV) surface analysis system that had a base operating pressure of $2 \times 10^{-10}$ Torr and was equipped with a quadrupole mass spectrometer (SRS RGA200), an ion sputter gun (PHI electronics), optics for low energy electron diffraction (LEED, OCI), and an HREEL spectrometer (LK Technologies). A Pt(111) single crystal that was 10 mm in diameter was used as a model catalyst. The Pt(111) sample was spot-welded to two tantalum wires that connected to a UHV sample manipulator which allowed it to be heated resistively and cooled to 110 K by conduction from a liquid N$_2$ reservoir. Prior to reactivity studies a clean and well-ordered Pt(111) surface was prepared by repeated cycles of 2 kV Ar$^+$ ion bombardment at 600 K for 40 min, followed with annealing at 1200 K in $2 \times 10^{-8}$ Torr O$_2$ and vacuum for 10 min respectively. Typically, six–eight cycles of this procedure were needed to achieve a clean Pt(111) surface.

Model CoPt bimetallic catalysts were prepared by vapor depositing Co atoms onto the Pt(111) surface using an evaporative Co source that consisted of a small coil of Co wire (Alfa Aesa, 99.995%) wrapped around a resistively-heated tungsten filament. The Co flux from the source was monitored using a quartz crystal microbalance located midway between the metal source and the sample, but positioned below the sample to avoid blocking of the flux of atoms to the Pt crystal. The interaction of Co atoms with a Pt(111) surface and the thermal stability of Co-modified Pt(111) surfaces has been previously studied by Chen and co-workers [23, 24]. In these studies it was shown that vapor-deposited Co atoms remain on top of the Pt(111) surface for temperatures below 700 K, while at higher temperatures they diffuse into the bulk. Since the goal of the present study was to assess how Co-addition to Pt affects reactivity through both electronic effects and by providing specific binding sites, we chose to use a Pt(111) surface that was decorated with Co adatoms as a model CoPt alloy surface. Such surfaces were easier to reproducibly prepare and control the number of exposed Co and Pt atoms compared to surfaces in which a portion of the Co was allowed to go sub-surface. A freshly prepared surface was used for each TPD run and HREELS temperature series.

The reactant, anisole (Sigma Aldrich, 99.7%), 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. A 0.6 L of anisole was used in both the TPD and HREELS experiments. This dosage was found to correspond to slightly greater than saturation coverage of anisole. A 3 K s$^{-1}$ heating rate was used for each TPD run, and the HREEL spectra were collected using a 4 eV electron beam oriented at 60° with respect to the surface normal. The resolution of each HREELS spectrum as determined by the full-width at half-maximum of the elastic peak was $\sim 40$ cm$^{-1}$.

**Results and discussion**

**Anisole reaction on Pt(111)**

To provide base case data we initially used TPD to investigate the adsorption and reaction of anisole on Pt(111). Figure 1 displays TPD data obtained from Pt(111) following 0.6 L exposure of anisole. The spectra contain a low-
temperature anisole peak centered at 235 K which corresponds to the desorption of physisorbed anisole, and a broad anisole peak centered at 375 K which corresponds to chemisorbed anisole molecules. Benzene was observed in a broad peak between 300–550 K, with the peak center near 430 K. Other than benzene, the only reaction products detected were CO and H2. The H2 was produced in two distinct peaks centered at 360 and 490 K, with a much broader feature spanning from 540–750 K. CO desorbed in two peaks centered at 430 and 490 K. With the exception that benzene was observed, these data are in agreement with that reported in our previous study[17]. These results are also similar to those reported previously by Réocreux et al [25] who also observed benzene as a product, although they reported only a single CO peak centered at 440 K. This difference may be related to the different anisole doses used in the two studies.

In our previous study[17] we concluded based on HREELS data that anisole undergoes O–CH3 bond cleavage on Pt(111) at temperatures as low as 250 K to form an oxocyclohexadienyl-structured intermediate (C6H6O) that bonds to the surface in an η5-π configuration. While the reader is referred to this previous study for a detailed analysis of the HREELS data that led to this conclusion, the most salient aspects of the analysis can be gleaned from the data in figure 2, which includes HREEL spectra for anisole-dosed Pt(111) at 115 and 300 K. The spectrum at 115 K is consistent with that expected for molecular anisole (see peak assignments in table 1). Heating to 300 K, however, results in significant changes in the spectrum of the adsorbed species including, most notably, the emergence of a peak at 1630 cm−1 which is characteristic of a ν(C=O) mode, the disappearance of the intense peak at 780 cm−1 which corresponds to the aromatic ring breathing mode of the intact anisole molecule, and a significant decrease in the intensity of the ν(C–H) mode at 3000 cm−1 which corresponds to the C–H stretching mode of the aromatic ring. All of these changes are consistent with cleavage of the O–CH3 bond to form the oxocyclohexadienyl intermediate. Ihm and White have previously reported that phenol also reacts on Pt(111) to form the same oxocyclohexadienyl intermediate [26]. For comparison, we have included in figure 2 an HREEL spectrum obtained in our laboratory for phenol-dosed Pt(111) heated to 300 K. The similarities between this spectrum and that of the anisole-dosed Pt(111) at 300 K are striking. Recently, based on DFT computational results Réocreux et al [25] also proposed that anisole reacts on Pt(111) to form a similarly-structured phenoxy-like intermediate that bonds to the surface via the aromatic ring. Together these results further confirm our assignment of the spectrum of the anisole-dosed surface to an oxocyclohexadienyl or similar phenoxy intermediate.

Our TPD and HREELS results show that the majority of the adsorbed oxocyclohexadienyl species derived from anisole undergo unselective decomposition to produce CO, H2, and adsorbed hydrocarbon fragments; however, as noted above, some benzene is produced during TPD in a broad peak between 300–550 K. It is noteworthy that a significant amount of CO is also produced in this temperature range (figure 1). Based on their DFT calculations, Réocreux et al [25] have proposed that the benzene producing pathway proceeds through an oxocyclohexadienyl species with cleavage of the Ph–O bond being facilitated by adsorbed methylidene or C

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**Figure 1.** TPD spectra obtained following exposure of the Pt(111) surface to 0.6 L of anisole.
Figure 2. HREEL spectra of oxocyclohexadienyl intermediate on Pt(111) and Co/Pt surfaces formed from anisole and phenol.

Table 1. Vibrational mode assignment.

| Mode                        | IR/Raman [28–30] | Pt(111) [17] | Zn/Pt(111) [17] | Co/Pt(111) |
|-----------------------------|------------------|--------------|------------------|------------|
| γ(C–C)\text{ring} (out of plane mode) | 509, 513         | 500          | 500              | 520        |
| Ring breathing              | 785              | 780          | 780              | 750        |
| γ(C–H)\text{ring} (out of plane mode) | 823, 859         | 820          | —                | —          |
| δ(C–H)\text{ring} (in plane mode) | 878, 894         | 880          | —                | —          |
| s(O–Me) + b(C–H)\text{ring} (out of plane mode) | 1022, 1029, 997 | 1010         | 1000             | 1030       |
| s(C–OMe) + s(C–H)\text{ring} (in plane mode) | 1182, 1183       | 1150         | 1150             | 1150       |
| δ(C–C)\text{ring} (in plane mode) + δ(C–H)\text{methyl} | 1453, 1436, 1468, 1422 | 1430         | 1440             | 1440       |
| s(C=O)                      | —                | 1550         | 1560             | 1560       |
| s(C=CH)\text{methyl}        | 2900             | 2870         | 2880             | 2880       |
| s(C–H)\text{ring}           | 3004             | 3000         | 3000             | 3000       |
| s(O–H)                      | —                | —            | 3500             | —          |
| s(Zn–O)                     | —                | —            | 400              | —          |
| s(Pt–C)                     | —                | 470          | 470              | 460        |

Note. s—symmetric, as—asymmetric, b—bend, ν—stretch, δ—deformation, ρ—rock, γ—wag, χ—scissor.
atoms which were formed as byproducts from the initial O–CH₃ bond cleavage as shown in figure 3. This pathway could therefore also be responsible for the low-temperature CO product observed in figure 1.

Anisole reaction on Co/Pt(111)

Similar to our previous studies of Zn-decorated Pt(111) surfaces [16, 18, 27], the addition of Co adatoms to the Pt(111) surface significantly altered the activity of the surface for the reaction of anisole. This is illustrated by the TPD data in figure 4, which was obtained from 0.4 ML Co/Pt(111) surface dosed with 0.6 L of anisole at 115 K. Consistent with the Co-free surface, anisole was observed to desorb in a narrow peak at 240 K and a somewhat smaller and broader peak at 370 K which can be attributed to physisorbed anisole, and chemisorbed anisole molecules, respectively. Hydrogen and carbon monoxide were the only other products observed with H₂ desorbing in two distinct peaks centered at 390 and 540 K, and a much broader peak from 600–770 K, and CO desorbing primarily in a peak centered at 430 K, with several minor peaks spanning from 500–800 K. Benzene was not observed as a product from the Co/Pt(111) surface.

To provide insight into the reaction pathways for anisole on 0.4 ML Co/Pt(111) and identify stable surface intermediates and their binding configurations, HREELS data for a 0.4 ML Co/Pt(111) surface dosed with 0.6 L of anisole were collected as a function of the surface temperature. These data are displayed in figure 5. Note that for each spectrum, the sample was heated to the indicated temperature and then rapidly quenched to 115 K, at which point the spectrum was collected. The spectra obtained at 145 and 200 K, which are below the desorption temperature of the physisorbed anisole, are consistent with those expected for molecular anisole. Individual peak assignments along with a comparison to those in the IR and Raman spectra of anisole [28–30] and the HREELS spectrum of molecular anisole on Pt(111), as reported in our previous study [17], are given in table 1.

Heating the surface to 250 K and then 350 K led to significant changes to the HREEL spectra. These include a large decrease in the intensity of the ring breathing mode at 750 cm⁻¹ and an increase in the intensity of a peak at 840 cm⁻¹ which has become the dominant peak between 500–1000 cm⁻¹. Peaks also emerged at 1630, 1800, and 2050 cm⁻¹, with the latter two corresponding to the ν(C=O) mode of CO adsorbed on Pt bridging and atop sites, respectively. Changes are also apparent in the C–H stretching region where the intensity of the ν(C–H)methyl peak (2880 cm⁻¹) increased relative to that of the ν(C–H)ring peak (3000 cm⁻¹). The appearance of the bridging and atop CO species indicates that unselective decomposition of some of the adsorbed anisole commences around 300 K. The other changes in the spectrum, including the emergence of a ν(C=O) peak at 1630 cm⁻¹, however, are comparable to those discussed above for the reaction of anisole on Pt(111) to form the oxycyclohexadienyl species. Indeed as shown in figure 2, the HREEL spectra for anisole-dosed Pt(111) and Co/Pt(111) after heating to 300 K are similar indicating that the oxycyclohexadienyl species is also formed on the Co/Pt(111) surface.

Figure 4. TPD spectra obtained following exposure of the Co/Pt(111) surface to 0.6 L of anisole.
While the two spectra clearly correspond to the same intermediate, it is noteworthy that the intensity of the \( \nu (C=O) \) peak at 1630 cm\(^{-1} \) is somewhat less in the spectrum from Co/Pt(111) compared to that from clean Pt (see figure 2). This change in peak intensity can be attributed to a difference in the bonding geometry for the oxocyclohexadienyl intermediate on the two surfaces. On Pt(111) bonding via the \( \pi \) electrons in the ring results in the C=O bond being tilted away from the surface as shown in figure 3 [17, 25, 26]. The decrease in the intensity of the \( \nu (C=O) \) peak for this intermediate on the Co/Pt(111) surface indicates that the C=O bond is now oriented more parallel to the surface. Such an orientation would result in an image dipole in the surface which counteracts that of the vibrational mode causing a decrease in the cross-section for exciting this mode. We postulate that this change in bonding configuration is a result of the oxygen in the carbonyl group interacting with an oxyphilic Co adatom on the Pt(111) surface as shown in figure 6. This conclusion is consistent with what we have observed previously for Pt(111) surfaces modified with oxyphilic Zn adatoms [17, 31] where the oxygens in both alcohols and carbonyl compounds preferentially bond to the Zn sites on these surfaces.

Heating the anisole-dosed Co/Pt(111) surface to 450 K produced additional changes in HREEL spectrum of the adsorbed intermediates, including the disappearance of the \( \nu (C=O) \) peak at 1630 cm\(^{-1} \), a large decrease in the intensity of the peaks between 1000–1500 cm\(^{-1} \), an increase in the intensity of the \( \nu (C-Pt) \) peak at 460 cm\(^{-1} \) due to both adsorbed CO and carbon, and an increase in the intensity of the \( \nu (C-O) \) peaks at 1800 and

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**Figure 5.** HREEL spectrum as a function of temperature for Co/Pt(111) dosed with 0.6 L anisole at 115 K.
While these changes may be partially due to some unselective decomposition of the oxocyclohexadienyl intermediate, the persistence of the intense peak at 840 cm\(^{-1}\) which is at an energy characteristic of the out-of-plane bending modes of an aromatic ring (see table 1) suggests that the ring structure remains intact. This observation along with the disappearance of the \(\nu(C\!=\!O)\) peak suggests that cleavage of the C–O bond in the oxocyclohexadienyl intermediate has occurred, resulting in the formation of adsorbed benzene or phenyl groups, as shown in figure 6.

To help verify this hypothesis, we compare the HREEL spectrum of the anisole-dosed Co/Pt(111) surface heated to 400 K with the HREEL spectrum of benzene on Co/Pt(111) at 300 K in figure 7. Except for the different intensities of the \(\nu(C\!=\!O)\) peaks at 1800 and 2050 cm\(^{-1}\) (the small C–O stretching peaks in the spectrum of the benzene-dosed sample are a result of CO adsorption from the background gas in the UHV chamber), the two spectra are quite similar. As discussed in the literature [32] the peaks at 1150 and 1440 cm\(^{-1}\) can be assigned to in-plane C–H and C–C modes. Since benzene adsorbs on Pt(111) with the aromatic ring parallel to the surface [32], these modes are oriented parallel to the surface which, due to the induced image dipole in the metal, have low excitation cross-sections. The similarity of these two spectra, therefore, provides support for the conclusion that on Co/Pt(111) the oxocyclohexadienyl intermediate undergoes C–O bond cleavage near 400 K to produce adsorbed benzene with the hydrogen required for this reaction being supplied by the unselective decomposition pathway. The adsorbed oxygen produced by this reaction appears to react with surface carbon which could also be produced by the unselective decomposition pathway to produce the CO that was observed at 430 K in the TPD experiment (figure 4).

Based on this analysis we propose the pathway depicted in figure 6 for the selective HDO of anisole on Co/Pt(111) to produce CO, H\(_2\) and adsorbed benzene. This pathway is similar to that proposed by Réocreux et al [25] for the reaction of anisole on Pt(111) (see figure 3) with the Co acting as the oxyphilic site that interacts with the

![Figure 6. Proposed reaction pathway for adsorption and reaction of anisole on Co/Pt(111) surface.](image)

![Figure 7. HREEL spectra of benzene intermediate on Co/Pt(111) surface formed from anisole or benzene.](image)
oxygen rather than an adsorbed C atom. We suspect that Co would be more effective in this role than C, but it is not possible to make this determination using the data obtained in the current study. It is also not clear why in the case of Pt(111) some of the benzene HDO product desorbs intact while for Co/Pt(111) it remains on the surface and decomposes at higher temperatures.

As noted in the introduction, our previous studies of the reaction of lignin-derived molecules on Zn-modified Pt(111) surfaces motivated the present study of the reaction of anisole on Co/Pt(111) with the goal of providing further insight into how oxyphilic modifiers on Pt influence the selectivity for HDO reactions [16–18]. Comparing the results obtained in the present study with those from our previous studies of Zn/Pt(111) reveals that the Zn and Co modifiers have some similarities, but there are also some significant differences. In both cases, the oxyphilic metals interact with the oxygen atoms in alkoxide groups in aromatic oxygenates, such as anisole, which helps facilitate C–O bond cleavage. The reaction pathways for anisole on Zn/Pt(111), however, are substantially different from those observed here for Co/Pt(111). In our previous studies we showed that, in addition to providing an adsorption site for the oxygen functionalities, Zn also has a strong electronic effect which destabilizes the bonding of aromatic rings with the Pt(111) surface [16–18, 27]. This destabilization is sufficient to change the most stable bonding configuration for anisole from one where the aromatic ring is situated parallel to the surface to one where the ring is tilted away from the surface. Indeed, on Zn/Pt(111), anisole adsorption occurs exclusively via interaction of the –O–CH₃ oxygen with a surface Zn site, with the aromatic ring tilted away from the surface. In the context of HDO catalysis, this is a desirable characteristic of the Zn modifier since it helps limit ring hydrogenation and enhances the selectivity for the production of the desired aromatic hydrocarbons as we have demonstrated in reactor studies with high surface area PtZn/C catalysts [17]. In contrast, the reaction of anisole on Co/Pt(111) is similar to that on the unmodified Pt(111) surface with the ring interacting strongly with the surface and cleavage of the O–CH₃ bond resulting in the formation of an oxocyclohexadienyl intermediate. This species then undergoes Ph–O bond cleavage which is mediated by Co or C sites on the Pt surface to produce benzene or an adsorbed phenyl group. Since Co addition does not destabilize the interaction of the ring with the Pt surface, Co/Pt catalysts are likely to promote both C–O bond hydrogenolysis and ring hydrogenation. A study by Do et al. on the HDO of m-cresol over PtCo/γ-Al₂O₃ which showed a high selectivity to methylcyclohexane supports this conclusion [22].

Conclusions

The results obtained in this study provide insight into the reaction of anisole on Pt(111) and Co-modified Pt(111) surfaces. On both surfaces, anisole undergoes O–CH₃ bond cleavage at relatively low temperatures to form an oxocyclohexadienyl-structured intermediate that bonds to the surface in a η₅-π configuration. Subsequent to this reaction, interaction of the O atom in oxocyclohexadienyl with oxyphilic Co and/or C sites on the Pt surface facilitates Ph–O cleavage to form adsorbed benzene or phenyl groups. In parallel with this reaction pathway unselective decomposition to produce adsorbed CO, H, and hydrocarbon fragments also occurs.

Comparing the results obtained here for Co-modified Pt(111) with those reported previously for Zn-modified Pt(111) reveals the both the Zn and Co atoms provide bonding sites for the oxygen in the alkoxide group in anisole which helps facilitate selective C–O bond cleavage. Zn was also found to have a strong electronic effect that destabilizes the interaction of aromatic rings with the Pt(111) surface, while a similar effect was not observed for Co.

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References

[1] Huber G W, Iborra S and Corma A 2006 Chem. Rev. 106 4044
[2] Gallego P 2012 Chem. Soc. Rev. 41 1538
[3] Stöcker M 2008 Angew. Chem., Int. Ed. 47 9200
[4] Chheda J N, Huber G W and Dumesic J A 2007 Angew. Chem., Int. Ed. 46 7164
[5] Alonso D M, Wettstein S G and Dumesic J A 2012 Chem. Soc. Rev. 41 8075
[6] Zakzeski J, Bruijnincx P C, Jongerius A L and Weckhuysen B M 2010 Chem. Rev. 110 3552
[7] Adler E 1977 Wood Sci. Technol. 11 169
[8] Bu Q, Lei H, Zacher A H, Wang L, Ren S, Liang X, Wei Y, Liu Y, Tang J and Zhang Q 2012 Bioresour. Technol. 124 470
[9] Centeno A, Laurent F and Delmon B 1995 J. Catal. 154 288
[10] Viljava T-R, Komulainen R and Krause A 2000 Catal. Today 60 83
[11] Wan H, Chaudhari R V and Subramaniam B 2012 Top. Catal. 55 129
[12] González-Borja M A and Resasco D E 2011 Energy Fuels 25 4155
[13] Sun J, Karim A M, Zhang H, Kovarik L, Li X S, Hensley A J, McEwen J-S and Wang Y 2013 J. Catal. 306 47
[14] Parsell T H, Owen B C, Klein I, Jarrell T M, Marcum C L, Haupert L J, Amundson L M, Kenntämaa H I, Ribeiro F and Miller J T 2013 Chem. Sci. 4 806
[15] Leng S, Wang X, He X, Liu L, Liu Y E, Zhong X, Zhuang G and Wang J-G 2013 Catal. Commun. 41 34
[16] Shi D and Vohs J M 2015 Surf. Sci. 650 161
[17] Shi D, Arroyo-Ramírez I and Vohs J M 2016 J. Catal. 340 219
[18] Shi D and Vohs J M 2017 Catal. Today 302 272
[19] Luo J, Yun H, Mironenko A V, Goulas K, Lee J D, Monai M, Wang C, Vorotnikov V, Murray C B and Vlachos D G 2016 ACS Catal. 6 6095
[20] Wang C, Luo J, Liao V, Lee J D, Onn T M, Murray C B and Gorte R J 2018 Catal. Today 302 73
[21] Wang G-H, Hilgert J, Richter F H, Wang F, Bongard H-J, Spleiethoff B, Weidenthaler C and Schüth F 2014 Nat. Mater. 13 293
[22] Do P T, Foster A J, Chen J and Lobo R F 2012 Green Chem. 14 1388
[23] Khan N A, Murillo L E and Chen J G 2004 J. Phys. Chem. B 108 15748
[24] Skopylak O, Menning C A, Barateau M A and Chen J G 2007 J. Chem. Phys. 127 114707
[25] Reocreux R, Ould Hamou C A, Michel C, Giorgi J B and Sautet P 2016 ACS Catal. 6 8166
[26] Ihm H and White J 2000 J. Phys. Chem. B 104 6202
[27] Shi D and Vohs J M 2015 ACS Catal. 5 2177
[28] Hoffmann L, Marquardt S, Gencmechu A and Baumgärtel H 2006 Phys. Chem. Chem. Phys. 8 2360
[29] Adams D M and Squire A 1974 J. Chem. Soc., Dalton Trans. 0 558–65
[30] Bloivo J, Biczysko M, Crescenzi O and Barone V 2008 J. Chem. Phys. 128 244105
[31] Martono E and Vohs J M 2013 J. Phys. Chem. C 117 6692
[32] Cenic F, Dippel O and Hasselbrink E 1995 Surf. Sci. 342 101