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Decomposition Pathways of C2 Oxygenates on Rh-modified Tungsten Carbide Surfaces

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Abstract

Ethanol decomposition on tungsten monocarbide (WC) and Rh-modified WC was investigated using ultrahigh vacuum (UHV) surface science experiments and density functional theory (DFT) calculations. DFT calculations indicated that the binding energies of ethanol and its decomposition intermediates on WC(0001) were modified by Rh, with Rh/WC(0001) showing similar values to those on Rh(111). Through temperature programmed desorption (TPD) experiments on polycrystalline WC and Rh-modified WC, it was shown that the selectivity for ethanol decomposition was different on these surfaces. On WC, the C-O bond of ethanol was preferentially broken to produce ethylene; on Rh-modified WC, the C-C bond was broken to produce carbon monoxide and methane. Furthermore, high-resolution electron energy loss spectroscopy (HREELS) was used to determine likely surface intermediates. On Rh-modified WC, ethanol first formed ethoxy through O-H scission, then reacted through an aldehyde intermediate to form the C1 products.

I. Introduction

Small-chain alcohols hold promise as renewable, energy-dense fuels and intermediates for the chemical industry. Significant research has been devoted to producing methanol and ethanol from biomass through direct and indirect routes [1]. For application to energy technologies, these alcohols can be reformed to produce H_2, and both direct methanol [2] and ethanol [3] fuel cells have been extensively studied. A potential class of catalysts for these applications is metal-modified carbides, which are useful materials for both catalysis and electrocatalysis [4]. In particular, metal-modified tungsten carbide (WC) has shown interesting properties regarding alcohol decomposition under ultrahigh vacuum (UHV) conditions. On polycrystalline WC, methanol underwent C-O bond scission to produce gas-phase methane and adsorbed oxygen [5]. Depositing one monolayer (ML) of Pt, Ni, or Rh completely shifted the selectivity of methanol decomposition to C-H cleavage, producing CO and H_2 [5, 6]. In the case of ethanol on WC and Ni/WC, ethylene was produced on WC and CO was produced on Ni/WC [7].

The results for ethanol decomposition on Ni/WC are promising for application to gas-phase reforming. However, Ni/WC is not a viable candidate for fuel cell applications, since Ni is unstable at anodic potentials in acidic conditions [8]. An electrochemically stable admetal that could be used is Rh, which is also interesting since it is very efficient at C-C bond cleavage. For example, a ternary electrocatalyst composed of Pt, Rh, and SnO_2 was shown to efficiently oxidize ethanol to CO_2 in acid electrolyte [9]. In UHV, the first step for ethanol decomposition on late transition metals has been reported as O-H rupture to form ethoxy [10-13]. On Pt(111), Ni(111), and Pd(111), the next bond to break was the α C-H bond, which formed an acetaldehyde intermediate [12-15]. However, ethanol followed a different pathway on Rh(111). In this case, the β C-H bond was cleaved to form a bidentate species known as an

oxametallacycle [10, 16, 17]. The bridge-like geometry of the oxametallacycle strained the C-C bond, leading to C-C rupture and CO formation at a temperature as low as 213 K [10]. In comparison, the C-C bond in the acetaldehyde intermediate on Pt, Ni, and Pd did not decompose until higher temperatures [11-13, 15]. An oxametallacycle intermediate was proposed on Rh(111) [18], which rapidly broke both C-C bonds to produce CO, H_2, and surface C.

In previous work for methanol decomposition on metal-modified carbides, Rh/WC was the most active surface [6]. Temperature programmed desorption (TPD) showed a higher production of CO and H_2 than the other metal-modified WC surfaces. Additionally, vibrational spectroscopy revealed that methanol decomposed by 200 K on Rh/WC, as compared to 300-400 K on the other surfaces. A significant question is whether Rh/WC possesses a high activity for decomposing the C-C bond in ethanol, which is required for its potential applications in both gas-phase reforming and electrooxidation of ethanol. Our current study of Rh/WC for ethanol decomposition uses both theoretical and experimental approaches. With density functional theory (DFT) we have calculated the binding energies of ethanol and some of its decomposition intermediates on WC and Rh-modified WC. Secondly, we have performed TPD and high-resolution electron energy loss spectroscopy (HREELS) in UHV to observe the reaction products and adsorbates as a function of temperature. Finally, we have also compared the vibrational spectra of acetaldehyde in order to determine the reaction mechanism.

II. DFT and Experimental Methods

2.1 DFT Calculations

Adsorbate binding energies were calculated on the closed-packed surfaces of WC(0001), Rh/WC(0001), and Rh(111) using DFT using the Vienna Ab-initio Simulation Package (VASP). The PW91 functional was used for electronic structure calculations [19-21]. Pseudopotentials

were used to represent the core electrons. A 3 x 3 hcp(0001) unit cell was used to represent the WC and Rh/WC surfaces, and a 3 x 3 fcc(111) structure was used for Rh. These calculations were done with a 3 x 3 x 1 k-point mesh. The energy cutoff was 396 eV and calculations were spin-polarized. Three WC layers were used in the calculations of WC(0001), with the bottom two layers fixed and the top layer allowed to relax. For the Rh/WC surface, a single monolayer of Rh was placed on the WC slab. For Rh(111), four Rh layers were used in the calculations, with the bottom two layers fixed and the top two layers allowed to relax. Binding energies were calculated by subtracting the clean slab and gas phase molecule energies from the slab-adsorbate energy.

2.2. UHV Techniques

A stainless steel UHV chamber was used for TPD experiments. The base pressure was 1 x 10^{-10} torr. The chamber was equipped with a sputter gun, a single-pass cylindrical mirror analyzer for Auger Electron Spectroscopy (AES), and a quadrapole mass spectrometer (QMS). Further details on the chamber can be found in previous publications [22, 23].

A separate UHV chamber was used for HREELS experiments, as described previously [24]. The chamber was equipped with a sputter gun, AES, QMS, and HREELS. The primary HREELS beam energy was 6 eV, and the angles of incidence and reflection were 60° with respect to the surface normal. The intensity of the elastic peak was in the order of 10^4 counts per second, and the spectral resolution was 45-55 cm^{-1}.

2.3 Preparation of WC and Rh-modified WC Surfaces

A polycrystalline W foil (Alfa Aesar, 99.95%) was spot-welded to two Ta posts, which served as electrical and thermal conductors. The temperature was varied within the range of

100-1200 K using liquid nitrogen cooling and resistive heating. A K-type thermocouple was spot-welded to the back of the foil to measure the temperature. The W foil was first cleaned by successive cycles of Ne^+ sputtering at 300 K and flashing to 1100 K. Once a clean surface was verified by AES, WC was synthesized by sputtering ethylene at 300 K. This was followed by flashing the foil to 1100 K to induce carburization, as described previously [25]. AES was used to verify a surface C/W stoichiometry of 1:1.

The clean WC surface was then modified by Rh using physical vapor deposition. A 0.5 mm W wire (Alfa Aesar, 99.95%) was wrapped with a 0.1 mm diameter Rh wire (Alfa Aesar, 99.8%). The Rh wire was heated to a desirable temperature to evaporate atomically clean Rh atoms onto the WC substrate. The WC substrate was held at 300 K during deposition. The coverage of Rh was estimated using the Rh/W AES peak intensity ratio [26].

Samples of ethanol (Sigma-Aldrich, 99.9+%) and acetaldehyde (Sigma-Aldrich) were purified by successive freeze-pump-thaw cycles. The WC substrate was cooled to 100 K before dosing the liquid sample. For TPD, the substrate temperature was then ramped from 100 to 800 K at a linear heating rate of 3 K/s, and desorption products were monitored by QMS. For HREELS, the substrate was flashed to different temperatures at a linear heating rate of 3 K/s. HREEL spectra were taken after the foil was cooled to 100 K.

III. Results and Discussion

3.1 DFT Calculations of Binding Energies

The binding of ethanol and ethoxy, a potential reaction intermediate, was calculated on the close-packed surfaces of WC, Rh/WC, and Rh. The binding geometry of ethanol on WC is shown in Figure 1. Ethanol adsorbed only in the atop position, with the O-H bond oriented parallel to the surface. Ethoxy was able to bind in all four surface sites: atop, fcc, hcp, and bridge. Ethoxy adsorbed in the hcp position on Rh/WC is illustrated in Figure 2. Table 1 shows the binding energy of ethanol and ethoxy on these surfaces. The binding energies of both species were consistent with previous studies in the case of WC [7] and Rh [27]. Also, binding energies followed the same trend of WC > Rh/WC > Rh observed for methanol and methoxy [6]. There is a difference of only 7 kcal/mol between the most stable binding energies of Rh and Rh/WC. It is thus expected that Rh/WC would exhibit similar activity to Rh. The binding energy of another potential intermediate, acetaldehyde, was also calculated. Two different binding configurations of acetaldehyde were studied, shown in Figure 3, with the C-O bond binding perpendicular to the surface in configuration η^1 and parallel to the surface in η^2. Table 2 summarizes the most stable binding sites and binding energy of each configuration on WC and Rh/WC. On both surfaces, the stable binding configuration was η^2. The binding energy for acetaldehyde is much lower than that of ethoxy, on both surfaces.

3.2 TPD and HREELS of Ethanol on WC and Rh/WC

The DFT predictions of different binding energies on WC and Rh/WC suggest that reaction pathways on the two surfaces may be different. Previous studies of oxygenates on metal-modified carbide surfaces have revealed that changes in adsorbate binding energy often lead to changes in the bond scission sequence [28, 29]. Rh/WC should be expected to show similar activity to Rh, since the binding energies of adsorbates on the two surfaces were similar.

In the current work, UHV studies were conducted to correlate the trends between binding

energy and bond scission sequence for C2 oxygenates on WC and Rh/WC. TPD spectra for ethanol on WC and Rh-modified WC, with different Rh coverages, are shown in Figure 4. H_2 was produced on all four surfaces, with a very broad desorption peak on clean WC. CO was produced on the Rh-modified surfaces, but not on clean WC. On clean WC, peaks were observed in both the 27 and 28 amu spectra at the same temperature of 375 K and with the same shape. The identities of these peaks were determined by dosing equal amounts of ethylene and CO into the UHV chamber in separate experiments. The intensity ratio of 27 and 28 amu of ethylene was found to be identical to that of the cracking pattern in Figure 4, indicating that the 28 amu peak was due solely to ethylene, and that no CO was produced on clean WC. The presence of ethylene as the dominant reaction product on WC indicates a selectivity towards C-O bond scission. A small amount of formaldehyde (mass 29 amu) was observed, but ethylene was the dominant product. After modifying the WC surface with Rh, ethylene production disappeared. Additionally, CO and CH_4 desorption products were observed. This shift in desorption products indicates that the Rh-modified surface is more active to C-H, and C-C bond scission than clean WC. This trend is similar to that observed for ethanol on Ni/WC [7].

The decomposition of ethanol can occur through the following four pathways.

Reforming	$aC_2H_5OH \rightarrow aCO + 3aH_2 + aC_{(ad)}$
Complete Decomposition	$bC_2H_5OH \rightarrow 2bC_{(ad)} + bO_{(ad)} + 3bH_2$
Methane Production	$cC_2H_5OH \rightarrow cCO + cCH_4 + cH_2$
Ethylene Production	$dC_2H_5OH \rightarrow dC_2H_4 + dH_2 + dO_{(ad)}$

The activity and selectivity towards these reactions were quantified using procedures described previously [7]. Table 3 shows the total activity, the sum of ethanol undergoing different pathways, and selectivity to each pathway. Clean WC showed higher total activity than any of the Rh/WC surfaces. On WC, the majority of ethanol underwent selective C-O bond scission to form ethylene, and the remainder underwent complete decomposition to atomic species. Adding submonolayer Rh shifted the selectivity toward the reforming and methane production pathways. Also, the total activity decreased with increasing Rh coverage. The product selectivity for ethanol decomposition was generally similar to that observed on Rh(111) [10, 16]. Unlike on Rh(111), methane production was observed on 0.5 ML and 1 ML Rh/WC. Methane was not observed in the TPD for 2 ML Rh/WC, similar to the results for Rh(111).

Further information for ethanol decomposition on Rh/WC was provided by HREELS. Figure 5 shows the HREEL spectra for 1 L ethanol on WC and 1 ML Rh/WC. The vibrational peak assignments are summarized in Table 4. On WC, the major peaks are as follows: δ(CCO), 507 cm^{-1}; $\gamma(CH_2)$, 798 cm^{-1}; ν_s(CCO), 873 cm^{-1}; ν_{as}(CCO), 1042; $\gamma(CH_3)$, 1366; $\gamma(CH_2)$, 1441; $\nu(CH_3)$, 2929; and ν(OH), 3200. The presence of the weak shoulder attributed to the O-H stretching mode indicates that at least a fraction of ethanol adsorbed molecularly, but also that a significant amount adsorbed dissociatively. This was consistent with earlier work of dissociative adsorption of methanol [5] and ethanol [7] on WC. Upon heating to 200 K, the vibrational peaks decreased uniformly. This trend continued through 400 K, but at 500 K, the peaks due to the C-C-O bond stretch disappeared. Taking into consideration of TPD detection of ethylene desorption in the range 300-550 K, the HREELS results suggest that the majority of ethoxy on the surface decomposed to form ethylene by 500 K.

On the ML Rh/WC surface at 100 K, a slight shoulder was observed at 3213 cm^{-1}, attributed to the presence of the O-H bond, indicating that at least a fraction of ethanol adsorbed molecularly, but the low intensity of the peak suggested that some adsorbed dissociatively as ethoxy. Likewise, both experimental [10, 16, 17] and theoretical [27, 30] work has shown that O-H cleavage was the first step for ethanol decomposition on Rh(111). After heating the Rh/WC surface to 200 K, the modes at 873 and 1042 cm^{-1} were no longer observed while the other peaks remained intact. Additionally, new peaks appeared at 1644 and 2009 cm^{-1}. The peak at 2009 cm^{-1} is adsorbed CO, and the peak at 1644 cm^{-1} is likely an aldehyde intermediate. No further changes occurred between 200 and 500 K. The disappearance of the C-C-O peaks and appearance of CO indicate a high activity for C-C bond cleavage on Rh/WC. On Rh(111), ethanol adsorbed molecularly and the O-H bond remained intact until 150 K. Additionally, the spectrum recorded at 213 K showed modes attributed to the C-C bond [10]. Rh/WC was thus more active than Rh(111) for both O-H and C-C bond cleavage.

3.3 Acetaldehyde on WC and Rh/WC

As discussed previously, ethanol did not react through an acetaldehyde intermediate on Rh(111). It was speculated that ethanol formed an oxametallacycle intermediate which weakened the C-C bond, but this intermediate is difficult to detect spectroscopically. To assess the bond scission sequence of ethanol on WC and Rh/WC surfaces, HREELS experiments were performed to study the adsorption and decomposition of acetaldehyde. Figure 6(a) shows the thermal sequence of acetaldehyde on clean WC. The vibrational peak assignments are in Table 3. The major peaks on WC are: δ(CCO), 528 cm-^{1}; ρ(CH_3), 886 cm^{-1}; ν(CC), 1123 cm^{-1}; δ(CH_3), 1360 cm^{-1}; ν(CO), 1427 cm^{-1}; ν(CH_3), 2949 cm^{-1}. Upon adsorption at 100 K on WC, the vibrational peaks were similar to that observed on Rh(111). Heating the surface to 200 K caused

very little change in the spectrum. Further heating to 300 K caused the C=O peak at 1651 cm^{-1} to decrease and shift to lower wavenumbers, suggesting that the C=O bond of acetaldehyde interacted with the surfaces through the η^2 configuration. This would agree with DFT calculations, which predicted that this configuration was the most stable. The similarity between the spectra of ethanol and acetaldehyde at 300 K suggests that they followed similar decomposition pathways on WC.

A comparison of the low-temperature spectra of ethanol and acetaldehyde on Rh/WC is shown in Figure 6(b). Unlike on WC, the C=O vibrational mode of acetaldehyde was not present near 1650 cm^{-1}, indicating that acetaldehyde adsorbed in the η^2 configuration. Comparing ethanol and acetaldehyde at 100 K, it is apparent that they existed as different species. However, at 200 K, adsorbed acetaldehyde shows generally similar features as ethanol; peaks due to C-C bond vibrations disappeared, and peaks due to adsorbed CO appeared. From these results, it appears that the ethanol decomposition pathway on Rh/WC is different from that on Rh(111). Similar to methanol on Rh/WC [6], it appears that the alkoxy intermediate decomposes through an aldehyde-like intermediate instead of an oxametallacycle. A fraction of this aldehyde fully dehydrogenated to form CO, but some remained as an aldehyde, leading to the peak at 1644 cm^{-1}. Based on the TPD results, some of this aldehyde species formed methane or CO, while the remainder underwent total decomposition.

Comparing to WC, the presence of Rh on WC significantly enhanced the C-C bond scission activity of ethanol. Although the C-C decomposition pathway on Rh/WC appeared to be different from the previously reported oxametallacycle intermediate on Rh(111), TPD results showed similar reaction products between the two surfaces. The facile C-C bond scission, combined with the electrochemical stability of WC [31] and Rh [9] in acid electrolyte, suggested

that monolayer Rh/WC can be a potentially active and lower-cost electrocatalyst for the electrooxidation of C2 oxygenates.

IV. Discussion

The differences in terms of activity and selectivity between WC and Rh/WC can be partially explained by comparing the adsorbate binding energies on the two surfaces. It was observed that WC had the highest total activity among the surfaces from TPD experiments, and that the adsorbate binding energies from DFT were highest on the bare WC slab. Upon Rh modification of the WC surface, the total activity decreased, but the reforming activity increased. DFT calculations showed that the ethanol and ethoxy binding energies were much lower on the ML Rh/WC slab as compared to the bare WC slab; the binding energies in this case were within 10% of those on Rh(111). The high binding energies on the WC surface suggests that adsorbates were more likely to react via bond breaking instead of desorption into the gas phase. In the opposite fashion, adsorbate bonds were selectively cleaved on the Rh/WC and Rh(111) surfaces, and the lower binding energies allowed these products to desorb. It was thus demonstrated that DFT calculation of binding energies can guide selection of catalyst materials for experimentation.

Conclusions

The decomposition of ethanol and acetaldehyde has been studied on Rh-modified WC. We have concluded the following based on these studies:

(1) Consistent with previous research, the first step for alcohol decomposition was breaking the O-H bond. Subsequently, ethanol reacted on bare WC to form ethylene through C-O scission.

Modification of WC with submonolayer amounts of Rh shifted the reaction selectivity towards C-H and C-C cleavage, giving CO and CH_4 as products.

(2) HREELS revealed that ethanol and acetaldehyde followed similar reaction pathways on both WC and Rh/WC. Ethanol reacted through α C-H scission to form acetaldehyde, instead of through β C-H scission to form an oxametallacycle. Both the HREEL spectra and DFT calculations suggested that acetaldehyde existed in the η^2 configuration, with the C-O bond parallel to the surface.

(3) The combined DFT and experimental results indicated that relatively simple DFT calculations, such as the binding energies of ethanol and key reaction intermediates, could provide useful guidance for selecting monolayer Rh/WC as a potential replacement to bulk Rh for the facile C-C bond scission of C2 oxygenates.

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Table 1. Binding energy of ethanol and ethoxy calculated by DFT. The text "ns" indicates that this was not a stable adsorption configuration.

Table 2. Binding energy of acetaldehyde and most stable binding site for the η^1 and η^2 conformations, as calculated by DFT.

Table 3. TPD quantification of ethanol on WC and Rh/WC surfaces. Numbers in parentheses indicate selectivity.

Table 4. HREELS vibrational assignments of ethanol on WC and Rh/WC. The text "nr" indicates that this vibrational mode was not resolved.

Table 5. HREELS vibrational assignments of acetaldehyde on WC and Rh/WC.

Table 1

	BE (kcal/mol)				
Surface	**Ethanol**	**Ethoxy**			
		Binding Site			
	atop	**atop**	**fcc**	**hcp**	**bridge**
WC(0001)	-17.28	-66.37	-74.84	-87.99	ns
Rh/WC(0001)	-10.49	-53.12	-56.00	-55.27	-54.55
Rh(111)	-9.64	-44.96	-47.17	-48.97	-44.22

Table 2

Surface	η^1		η^2	
	Binding Site	**BE (kcal/mol)**	**Binding Site**	**BE (kcal/mol)**
WC(0001)	atop	-15.70	bridge	-49.96
Rh/WC(0001)	atop	-7.68	atop	-11.36

Table 3

	Activity (ML)					
surface	**reforming**	**decomposition**	**CH_4**	**Ethylene**	**Formaldehyde**	**total**
WC	0	3.0×10^{-2} (32.1)	0	6.4×10^{-2} (67.3)	6.0×10^{-4} (0.63)	9.5×10^{-2}
0.5 ML Rh/WC	2.7×10^{-2} (32.9)	1.9×10^{-2} (23.2)	3.5×10^{-2} (42.7)	1.4×10^{-3} (1.2)	0	8.2×10^{-3}
1 ML Rh/WC	2.1×10^{-3} (15.7)	3.2×10^{-3} (23.9)	8.1×10^{-3} (60.4)	0	0	1.3×10^{-2}
2 ML Rh/WC	1.1×10^{-3} (12.6)	7.6×10^{-3} (87.4)	0	0	0	8.7×10^{-3}

Table 4

	Ethanol HREELS assignments, frequency (cm^{-1})				
mode	**gas phase[a]**	**solid phase[b]**	**Rh(111)[c]**	**WC**	**Rh/WC**
ν(MC), M-CO			470		419
δ(CCO)		419	480	507	440
$\gamma(CH_2)$		801	815	798	798
ν_s(CCO)	880	885	890	873	873
$\rho(CH_3)$		1033	nr	nr	nr
ν_{as}(CCO)	1060	1089	1070	1042	1042
γ(OH)		1241	815		nr
$\delta(CH_3)$	1390	1452/1394	1380	1366	1360
$\delta(CH_2)$	1450	1490	1490	1441	1441
ν(CO), M-CO			2030		2009
$\nu(CH_2)$		2900	nr	nr	nr
$\nu(CH_3)$	2965/2880	2989/2943	2990	2929	2929
ν(OH)	3660	3676	3270	3200	3213

[a]Ref. [32]
[b]Ref. [33]
[c]Ref. [10]

Table 5

Acetaldehyde HREELS assignments, frequency (cm^{-1})				
mode	solid phase[a]	Rh(111)[b]	WC	Rh/WC
δ(CCO)	522	610	528	528
ρ(CH_3)	882	950	886	886
ν(CC)	1118	1135	1123	1116
δ(CH_3)	1431/1389	1380	1360	1346
ν(CO), aldehyde	1722	1460	1427	1420
ν(CH_3)	2964/2918	2980	2949	2963

[a]Ref. [34]
[b]Ref. [10]

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Figure 1. Side (a) and top (b) views of ethanol adsorbed in the atop position on WC(0001). Atom colors are as follows: Green = W, Blue = C, Red = O, and White = H.

Figure 2. Side (a) and top (b) views of ethoxy adsorbed in the hcp position on Rh/WC(0001). Atom colors are as follows: Green = W, Gray = Rh, Blue = C, Red = O, and White = H.

Figure 3. Acetaldehyde adsorbed in the η^1 (a) and η^2 (b) configurations on WC(0001). Atom colors are as follows: Green = W, Blue = C, Red = O, and White = H.

Figure 4. Comparison of TPD spectra of reaction products H_2, CO, CH_4, and C_2H_4 from the decomposition of ethanol on WC and Rh/WC.

Figure 5. Comparison of HREELS spectra of ethanol on WC and Rh/WC.

Figure 6. Comparison of HREELS spectra of acetaldehyde on WC and Rh/WC.

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