ACS Catalysis
Cite This: ACS Catal. 2018, 8, 10089−10095
Research Article
pubs.acs.org/acscatalysis

Energetics of Adsorbed Methanol and Methoxy on Ni(111): Comparisons to Pt(111)

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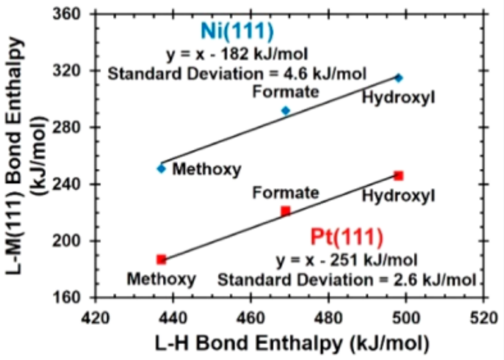
Supporting Information

ABSTRACT: The heats of adsorption of methanol molecularly adsorbed on clean Ni(111) and dissociatively adsorbed on oxygen-precovered Ni(111) were measured by single-crystal adsorption calorimetry (SCAC). The dissociative adsorption of methanol on oxygen-precovered Ni(111) produces adsorbed methoxy and hydroxyl, resulting in an integral heat of adsorption of −70. kJ/mol at a coverage of 0.25 ML. From this, the heat of formation of this adsorbed methoxy and the dissociation enthalpy of its bond to Ni(111) are estimated to be −233 and 250. kJ/mol, respectively. Analyzing previously measured bond enthalpies of monodentate formate and hydroxyl to Ni(111), we find a linear trend with a slope of 1 between the bond enthalpies of oxygenates to the Ni(111) surface and their corresponding gas-phase hydrogen−ligand bond dissociation enthalpies, similar to the trend for Pt(111) but ~69 kJ/mol stronger. We also compare our experimentally measured energetics for adsorbed methanol and adsorbed methoxy with density functional theory (DFT) calculations with periodic boundary conditions from previous literature. These energetic values and trends help clarify selectivity, reaction rate, and activity differences between metal surfaces in reactions involving adsorbed oxygenates.



KEYWORDS: *adsorption energy, methanol, Ni(111), calorimetry, catalyst*

INTRODUCTION

Surface methoxy is a key intermediate in many important catalytic reactions on Ni and other transition metal surfaces, such as steam reforming reactions, methanol synthesis, and direct alcohol fuel cell reactions. Critical catalytic properties, such as the activity, reaction rate, and selectivity, are determined by the energetics of adsorbed intermediates, and they are therefore important to know accurately. The adsorption and decomposition reactions of methanol on Ni(111) have been studied previously.[1−10] However, little is known about the energetics of adsorbed methanol and methoxy on this or any other Ni surfaces. So far, the heat of formation and bond enthalpy of adsorbed methoxy have been measured on only one metal surface, Pt(111), using single-crystal adsorption calorimetry (SCAC) by this group.[11] Here, we report the first calorimetric measurements of the energetics of adsorbed methanol and methoxy on the Ni(111) surface. These energetics are compared to adsorbed methoxy on Pt(111), helping clarify the different catalytic activities for these two transition metals in catalytic reactions involving methoxy intermediates. These experimental results also provide valuable benchmarks for validating the energy accuracy of density functional theory (DFT) methods.

In addition, we compare here the energetics of adsorbed hydroxyl and formate on Ni(111), reported by our group previously,[12,13] with the measurement of adsorbed methoxy here, and find the bond dissociation enthalpies of these three adsorbed oxygenates (hydroxyl, formate, and methoxy) to Ni(111) linearly track their corresponding gas-phase hydrogen−ligand bond dissociation enthalpies with a slope of 1. The same trend with unit slope was also discovered for these same three oxygenates on Pt(111) by this group previously.[14] The difference is that these three oxygenates bind to Ni(111) ~69 kJ/mol more strongly than Pt(111). These findings thus provide a semiempirical method to predict the bond enthalpies and heats of formation of adsorbed oxygenates on these metal surfaces.

Previous studies have found that methanol adsorbs molecularly on Ni(111) below approximately 140 K.[5,10] Adsorbed methoxy has been observed on Ni(111) after dosing high coverages (possibly multilayers) of methanol at temperatures lower than 140 K and subsequently heating to 160−240 K.[3−5,8−10] Although not known from the literature, we show below that when methanol is dosed to Ni(111) precovered with oxygen adatoms, it dissociates to produce adsorbed methoxy plus −OH in the temperature range 100−190 K. This is based on the similarities of heats of reaction and sticking probabilities versus oxygen coverage to prior results for

Received: July 28, 2018
Revised: September 15, 2018
Published: September 18, 2018

DOI: 10.1021/acscatal.8b02992
ACS Catal. 2018, 8, 10089−10095

Pt(111), where this reaction is known to occur at similar temperatures.[12]

■ EXPERIMENTAL SECTION

Experiments were performed in a UHV chamber (base pressure < 2×10^{-10} mbar) designed for SCAC. It is equipped with X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low-energy ion scattering spectroscopy (LEIS), and low-energy electron diffraction (LEED). The apparatus and procedures for SCAC have been described in extensive detail previously.[15−17] To summarize, the Ni(111) samples used in these experiments are 1 μm thick single-crystal foils and were provided by Jacques Chevallier at Aarhus University. The surface was cleaned by cycles of Ar^+ ion sputtering and annealing to 1120 K. The atomic oxygen-precovered surface was prepared by exposing the clean Ni(111) surface to O_2 at cryogenic temperatures (100−190 K) as described in the literature.[18−20] The heats of adsorption and sticking probability were measured simultaneously as a pulsed molecular beam of methanol was dosed onto the Ni surface. The molecular beam was created by expanding ∼2 mbar of methanol through a glass capillary array and collimated through a series of five orifices that are cooled with liquid nitrogen, and then chopped into 102 ms pulses. The heats were measured with a pyroelectric ribbon gently pressed on the backside of the Ni crystal. The short-term and long-term sticking probabilities were measured with a quadrupole mass spectrometer (QMS) using the King and Wells method.[21]

In this Article, we report coverages in monolayers (ML), which are defined as the number of methanol molecules that adsorb to the surface irreversibly, normalized by the number of nickel surface atoms in the Ni(111) surface (1.86×10^{15} Ni atoms/cm^2). A typical molecular beam flux gives ∼0.015 ML per pulse (∼4.2×10^{12} molecules/pulse).

■ RESULTS

Heat of Molecular Adsorption on Clean Ni(111). In this Article, we define the term heat of adsorption as the negative of the differential standard molar enthalpy change for the adsorption reaction, $-\Delta H_{ad}$, with the gas and the metal surface being at the same temperature as the metal surface. ("Standard" here implies only that the gas is at 1 bar as a pure ideal gas.) As described previously, this requires a small enthalpy correction on the measured heat because the gas molecule's enthalpy at this temperature is slightly different from the actual experimental molecular beam conditions.[22]

According to the literature,[2,5] methanol molecularly adsorbs on Ni(111) below 160 K and forms multilayers below 140 K. Figure 1 shows the heat of adsorption of methanol on Ni(111) at 100 K. Initially, methanol adsorbs molecularly with a heat of adsorption of 63.2 ± 0.8 kJ/mol in the limit of low coverage. As coverage increases to 0.4 ML, the heat of adsorption decreases in two linear segments. For the first 0.3 ML, the heat of adsorption is well described by a best fit line (63.2−23.9 θ) kJ/mol, where θ is coverage, in monolayers, yielding an average heat of 59.6 kJ/mol. The average (or integral) heat of adsorption up to 1/4 ML is 60.2 kJ/mol. Combined with the standard heat of formation of methanol gas of −202 kJ/mol,[23] this gives the standard heat of formation of adsorbed methanol on Ni(111) to be −262 kJ/mol. After 0.30 ML and up to 0.4 ML, the heats of adsorption decrease much more rapidly and are well described by the best-fit line (99.3−142.7 θ) kJ/mol. The sticking probability of methanol is always close to unity at all methanol coverages at 100 K; see Figure S1.

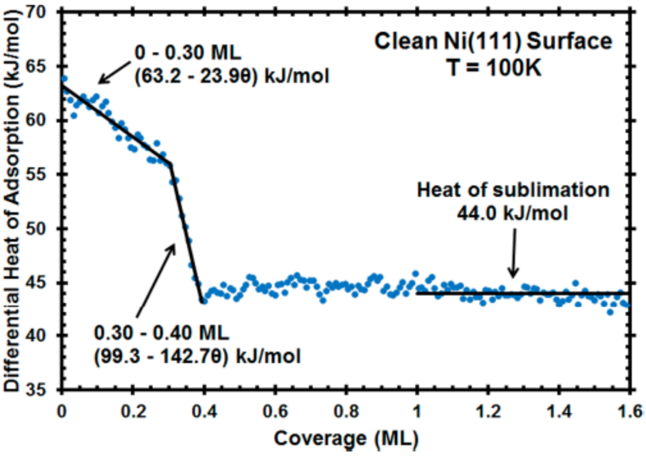


Figure 1. Differential heat of adsorption of methanol on the clean Ni(111) surface as a function of methanol coverage at 100 K.

These changes in the heat of adsorption could be the result of a model suggested by scanning tunneling microscopy (STM) and DFT studies of methanol on Cu(111), Au(111), and Pt(111).[24−26] On these surfaces at cryogenic temperatures, the methanol molecules bind to the surface through their oxygen atom but with the methyl group near the surface, forming hydrogen bonds with their neighbors. This results in clusters of hydrogen-bonded hexamers at low coverages and long hydrogen-bonded chains at higher coverages with the methyl groups pointing outward. One STM study found that these methanol chains get closer to one another as coverage increases.[24] The decrease in heat with coverage in Figure 1 may be due to dipole−dipole and steric repulsions between chains and hexamers as they are forced closer together.

At coverages greater than 0.4 ML, the heat of adsorption becomes nearly constant, implying that additional methanol adsorbs on top of methanol adsorbates, forming multilayers. Above 1.0 ML, the multilayer adsorption energy is 44.0 ± 0.6 kJ/mol. This value is in agreement with the heat of sublimation of bulk methanol (solid) at 100 K, 45.3 kJ/mol, calculated from bulk thermodynamic data,[27,28] and with results from a detailed TPD study of multilayer methanol on Au(111) that employed leading edge analysis to determine a sublimation enthalpy of 42.1−44.6 kJ/mol[29] (after correction using bulk solid and gas-phase heat capacities from 150 to 100 K).

Previous literature reported that exposing a clean Ni(111) surface to a high coverage of methanol at a temperature lower than 140 K and subsequent heating to 180−240 K leads to adsorbed methoxy and hydrogen.[5,10] Amemiya and co-workers determined that methoxy could also be produced on Ni(111) by directly dosing methanol at 200 K.[10] Thus, we performed SCAC experiments of methanol adsorption on clean Ni(111) at temperatures ranging from 180−300 K in hopes to produce adsorbed methoxy. However, we observed an initial heat of adsorption that was very similar to that for molecular adsorption of methanol on Ni(111) at 100 K (∼63 kJ/mol) and a maximum surface coverage of adsorbed methanol (regardless the products on surface) of ≤0.04 ML at 180−300 K. It indicates that methanol transiently adsorbs on Ni(111) at these temperatures, but then desorbs again before the next methanol pulse. Thus, we were unable to dissociate the methanol on clean Ni(111). In at least some of the prior studies mentioned above, it was possible that photon or electron beam damage (e.g., from X-rays in XPS or electrons from mass spectrometer filaments) may have facilitated dissociation.

Heat of Dissociative Adsorption of Methanol on Oxygen-Predosed Ni(111). After predosing the Ni(111) surface with oxygen adatoms (by the dissociative adsorption of O_2 gas), the heat of adsorption of methanol at temperatures from 100 to 190 K is considerably higher than the heat of molecular adsorption (~25 kJ/mol higher initially), and the resulting coverage of permanently adsorbed methanol is much higher. According to the studies of methanol dissociatively adsorbing on O-precovered Pt(111)[11] and water dissociatively adsorbed on O-precovered Ni(111),[12] we thus conclude that reaction 1 occurs to produce adsorbed methoxy and hydroxyl, as

$$CH_3OH_g + O_{ad} \rightarrow CH_3O_{ad} + OH_{ad} \tag{1}$$

Figure 2 shows the heat of adsorption of methanol on oxygen-precovered Ni(111) at 100 K with 0.25 ML of O_{ad} (red squares) and a low coverage of O_{ad} (black triangles). The heat of adsorption of molecular methanol on clean Ni(111) at 100 K is also reproduced from Figure 1 (blue circles), for comparison. When the Ni(111) surface is covered with 0.25 ML of O_{ad}, a significantly higher heat of adsorption is observed, ~88 kJ/mol in the limit of low coverage. This heat then decreases linearly with increasing coverage of adsorbed methanol. After ~0.25 ML, the heat of adsorption is the same as that of methanol molecularly adsorbed on clean, O-free Ni(111), suggesting that methanol molecularly adsorbs from 0.25 ML until saturation at ~0.3 ML. In the case of the low coverage of O_{ad}, the heat of adsorption of methanol starts high, close to the curve for 0.25 ML O_{ad}, and more quickly decreases to the same heat as that of molecular adsorption on O-free Ni(111) (the blue curve) at ~0.1 ML. This shows that the coverage dependence of the heats of adsorption of methanol on O-precovered Ni(111) significantly depends on the precoverage of O adatoms, again implying that methanol reacts with O adatoms to form adsorbed methoxy and hydroxyl until all of the O_{ad} is consumed. This same reaction was observed on Pt(111) with similar heats.[11]

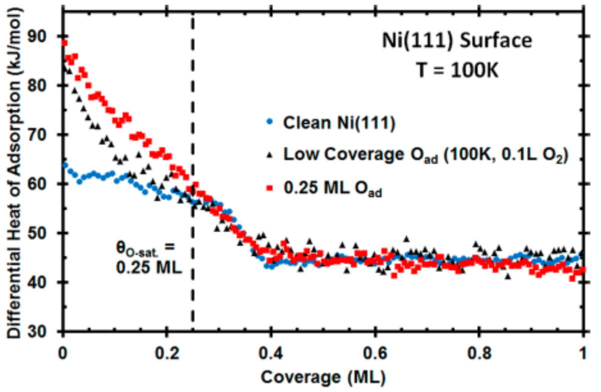


Figure 2. Differential heat of adsorption of methanol on Ni(111) at 100 K versus total methanol coverage. Each curve represents a different coverage of predosed oxygen adatoms on the surface, including the clean, O-free surface, a low coverage of O_{ad}, and 0.25 ML of O_{ad}. The vertical dashed line at 0.25 ML is where the reaction of methanol with O_{ad} to produce $CH_3O_{ad} + OH_{ad}$ is expected to finish for this highest predose of O_{ad}.

The heats of adsorption observed at low coverage on the 0.25 ML O_{ad} surface are much higher than what would be expected for simple molecular adsorption. On both Pt(111) and Ni(111), water molecularly coadsorbed with oxygen adatoms releases only ~3 kJ/mol more heat as compared to the molecular adsorption of water on clean surfaces.[12,30] We would expect a similar marginal change in heat if methanol molecularly coadsorbed with O_{ad}. In contrast, here the heat is ~25 kJ/mol higher for methanol adsorbed on the O-precovered surface at the limit of low coverage as compared to the clean Ni(111), which indicates dissociative adsorption on O-precovered Ni(111). We attribute this much higher heat to methanol reacting with O_{ad} to form adsorbed methoxy and hydroxyl following reaction 1. This reaction has also been unambiguously observed on O-precovered Pt(111).[11,31] We expect reaction 1 to proceed until all oxygen is titrated off the surface, after which methanol continues to adsorb molecularly and releases the same heat as on clean Ni(111). For the 0.25 ML O_{ad} precovered surface, this reaction completes at ~0.25 ML as expected; for the low coverage experiments, this higher-heat reaction completes at ~0.1 ML (Figure 2). We are unsure of the structure of the molecularly adsorbed methanol that populates after all 0.25 ML of the O_{ad} is consumed by reaction 1, but its heat quickly drops to that for multilayer methanol by 0.4 ML. It is not clear why the coverage dependence of the heat in this range from 0.25 to 0.4 ML is so similar to that without 0.25 ML of predosed oxygen adatoms.

Figure 3 shows the more direct comparison for methanol adsorbed on Ni(111) and Pt(111), dissociatively and molecularly. The red curves show SCAC results of methanol on both Ni(111) and Pt(111) predosed with 0.25 ML O_{ad}, and the blue curves show SCAC results of methanol on clean Ni(111) and Pt(111). The two curves shown for Pt(111) were

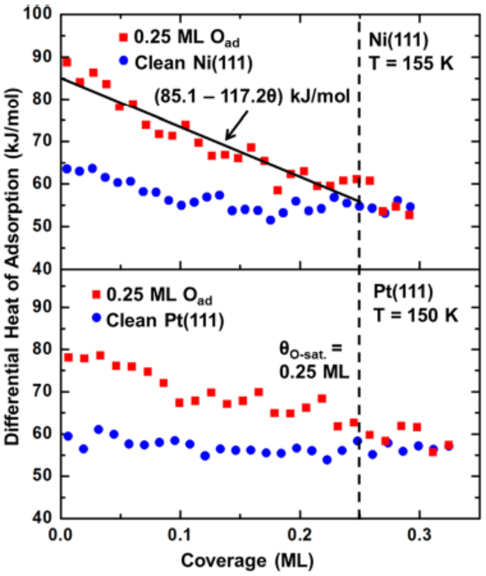


Figure 3. Differential heat of adsorption of methanol versus total methanol coverage on Ni(111) at 155 K and on Pt(111) at 150 K at two surface conditions: the clean metal surface and with 0.25 ML precoverage of O_{ad}. The vertical dashed line at 0.25 ML is where the reaction of methanol with O_{ad} to produce $CH_3O_{ad} + OH_{ad}$ is expected to finish.

DOI: 10.1021/acscatal.8b02992
ACS Catal. 2018, 8, 10089−10095

published previously[11] and reproduced here for comparison. On Pt(111), a reaction scheme identical to that proposed here for Ni(111) is known to occur.[11] On clean Ni(111) at 155 K and clean Pt(111) at 150 K, methanol adsorbs molecularly and only forms a single layer, and the heats are consistent with the adsorption on clean surfaces at 100 K.[2,31] For the 0.25 ML O-precovered surfaces, methanol reacts with O_{ad} forming adsorbed methoxy and hydroxyl until the 0.25 ML of O_{ad} is titrated. After that, methanol continues to adsorb molecularly until the saturation coverage for that temperature is reached, releasing the same heat as observed on the clean surfaces at the same coverages. On the O-precovered surface on Ni(111), the heat of adsorption is initially 87 kJ/mol at the limit of low coverage. It decreases linearly until ∼0.25 ML and is well described by the linear fit $(85.1-117.2\,\theta)$ kJ/mol. The vertical dashed line at 0.25 ML marks the expected coverage of O_{ad} and represents the point where reaction 1 completes. After this vertical dashed line, it is clearly observed that the heat of adsorption of methanol on the oxygen-precovered surface has decreased to be the same as that on clean Ni(111) at higher coverages. Methanol saturates at ∼0.3 ML (see Figure S1 for related sticking probability data) for the single layer of adsorbates on Ni(111) at 155 K, smaller than Pt(111) at 150 K (∼0.33 ML),[11] which is expected due to Pt(111) having a larger lattice parameter and 19% smaller density of surface atoms than Ni(111).

Further evidence for the formation of methoxy is shown in Figure S2, which shows the SCAC results for methanol adsorption onto O-precovered Ni(111) at 190 K. Here, we observe the same heats as the O-precovered Ni(111) surface at 100 and 155 K, but a lower final coverage of ∼0.16 ML, due to a lower predosed coverage of O_{ad} (see also Figure S1).

■ DISCUSSION

Energetics of Adsorbed Methoxy. From the heats of adsorption measured in this work by calorimetry and the available literature values for the heats of formation of adsorbed and gas-phase species, we may extract the heat of formation of methoxy on Ni(111) and its bond enthalpy to this surface. We attribute the integral heat of adsorption from 0−0.25 ML on the 0.25 ML oxygen-precovered Ni(111) surface at 155 K (Figure 3) of −70. kJ/mol to the heat of reaction 1. Figure 4 shows the thermodynamic cycle, which uses this integral heat to extract the heat of formation of adsorbed methoxy and the $CH_3O-Ni(111)$ bond dissociation enthalpy, $D(CH_3O-Ni(111))$.

This thermodynamic cycle starts on the left-hand side with all atoms in their standard state, which therefore possesses an enthalpy of formation of 0 kJ/mol. Following the bottom path shows the formation of gaseous methanol and an adsorbed oxygen atom, which possess enthalpies of formation of −202 and −240. kJ/mol, respectively.[22,23] The bottom path then tracks the dissociative adsorption of methanol to make adsorbed methoxy plus adsorbed hydroxyl, the enthalpy of which we measured with calorimetry (−70. kJ/mol). This is an exothermic process and the enthalpy of reaction is a negative value, while the values shown in Figure 3 are the heats of adsorption, which, by convention, are shown as positive values. Combining the heats of formation and measured reaction enthalpy of the bottom path results in the total heat of formation of coadsorbed methoxy and hydroxyl, both at 0.25 ML coverage, a value of −512 kJ/mol.

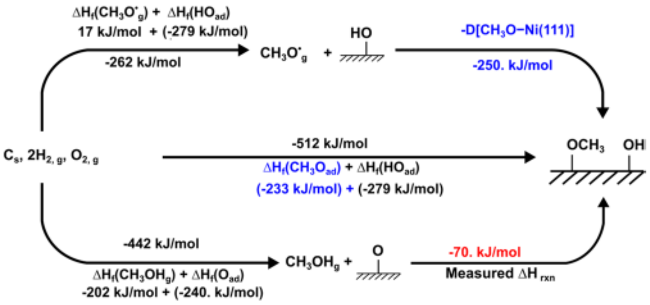


Figure 4. Thermodynamic cycle used to calculate the heat of formation and bond dissociation enthalpy of adsorbed methoxy to the Ni(111) surface, which are shown in blue. The red value of −70. kJ/mol is the measured enthalpy of reaction of gaseous methanol onto the surface precovered with 0.25 ML of O_{ad} at 100 K producing adsorbed methoxy and hydroxyl. This is the integral or average reaction enthalpy from 0 to 0.25 ML of dissociatively adsorbed methanol. The other values shown in black are from the literature, as described in the text.

The middle path in the thermodynamic cycle (Figure 4) shows this enthalpy change of converting all atoms in their standard states directly to coadsorbed methoxy and hydroxyl. Therefore, the sum of their enthalpies of formation must be equal to the total heat of formation (−512 kJ/mol). The enthalpy of formation of hydroxyl at 0.25 ML on Ni(111) was previously measured to be −279 kJ/mol.[12] Subtracting this enthalpy of formation of adsorbed hydroxyl from the total enthalpy of formation results in the enthalpy of formation of adsorbed methoxy at 0.25 ML coverage: −233 kJ/mol.

Following the top pathway on this thermodynamic cycle (Figure 4) shows the method to extract the bond enthalpy of methoxy to Ni(111). This top route starts by converting the standard state elements to a gaseous methoxy radical and an adsorbed hydroxyl, which possess an enthalpy of formation of +17 and −279 kJ/mol, respectively.[12,32] These two species have a total enthalpy of formation of −262 kJ/mol. The difference in enthalpies between these two species and our final state on the far right is negative of the adiabatic $CH_3O-Ni(111)$ bond dissociation enthalpy. Therefore, +250. kJ/mol is the enthalpy for breaking the $CH_3O-Ni(111)$ bond at 0.25 ML coverage (when coadsorbed with 0.25 ML of hydroxyl).

Comparison to DFT Calculations. The bond energy of molecular methanol and methoxy to Ni(111) measured here may be compared to theoretical calculations. Table 1 compares computational values obtained by various DFT methods to the experimental values of this work. DFT calculations report integral bond energies of adsorbates at specific coverages. To calculate the bond energy of molecular methanol at a specific coverage, the best-fit line of the measured differential heats of methanol adsorption versus coverage from 0 to 0.30 ML at 100 K (Figure 1) was integrated up to the desired coverage. These integral heats (enthalpies) were then converted to bond energies by subtracting RT. The calorimetric bond enthalpies for methoxy at the different coverages in Table 1 were calculated from thermodynamic cycles similar to that in Figure 4 discussed above, but by integrating to different coverages to calculate the integral heat of reaction at that coverage, using the reported heat of formation of adsorbed hydroxyl at that coverage.[12] Again, bond enthalpies were converted to bond energies by subtracting RT.

For molecular methanol, all reported DFT calculations significantly underestimated the bond energy measured in this

DOI: 10.1021/acscatal.8b02992
ACS Catal. 2018, 8, 10089−10095

Table 1. Comparison of the Present Calorimetric Integral Bond Energies of Methanol to the Ni(111) Surface with Calculated Values Using DFT with Periodic Boundary Conditions

molecularly adsorbed methanol			bond energy (kJ/mol)		ref
coverage	DFT functional/method	DFT site	DFT	calorimetry	DFT
1/9 ML	PW-91	top	24	61	35
1/9 ML	PW-91	top	32	61	34
1/6 ML	PBE	top	16	60	36
1/4 ML	RPBE	top	2	59	33
	methoxy		bond energy (kJ/mol)		ref
coverage	DFT functional/Method	DFT site	DFT	calorimetry	DFT
1/9 ML	PW-91	hollow	257	257	35
1/9 ML	PW-91	FCC hollow	243	257	34
1/6 ML	PBE	FCC hollow	249	254	36
1/6 ML	PW-91	FCC hollow	264	254	37
1/4 ML	RPBE	top	180	249	33

work. The weaker bond strength found in these DFT studies than by calorimetry could be due to methanol forming hydrogen-bonded structures, similar to what has been observed in Cu(111) and Au(111).[24,25] These intermolecular hydrogen bonds may not be properly accounted for as these chains would have significantly larger unit cells than what was used in these calculations. These underestimations in bond energy could also be due to underestimating the magnitude of van der Waals and dipole interactions between the adsorbate and the surface. For adsorbed methoxy, PW-91 and PBE perform well, differing from the experimentally determined value by only 0–14 kJ/mol. However, RPBE underestimates the bond energy by 69 kJ/mol. This RPBE paper only reported their calculated results on top sites.[33] Their value of 180 kJ/mol is close to the reported energies of methoxy bound to top sites by another DFT functional, PW-91 (175 kJ/mol).[34]

Comparison to Pt(111). Previous work[11] from this research group studied the adsorption of methanol and methoxy on Pt(111), allowing for a direct comparison between the two metal surfaces. These values are adjusted slightly (by a value of RT_{source}) from the literature to account for a systematic error as discussed elsewhere.[22] Methoxy on Pt(111) at 0.25 ML coverage coadsorbed with 0.25 ML of hydroxyl has a heat of formation of −168 kJ/mol (as compared to −233 kJ/mol on Ni(111) under the same conditions) and a bond enthalpy of −185 kJ/mol (as compared to −250. kJ/mol on Ni(111) under the same conditions). These much larger values on Ni(111) are to be expected as it is well-known that Ni is more oxophillic than Pt, so that Ni–O bonds should be stronger.

It is interesting to consider how these energetic differences between Ni and Pt manifest themselves in catalysis. Let us consider a simple reaction involving C–O bond cleavage:

$$CH_3O_{ad} \rightarrow CH_{3,ad} + O_{ad} \quad (2)$$

Using the published heats of formation of $CH_{3,ad}$ + O_{ad} of −71 kJ/mol[38] and −240. kJ/mol,[22] respectively, together with the heat of formation of CH_3O_{ad} on Ni(111) of −233 kJ/mol found above gives a highly exothermic enthalpy for reaction 2 of −78 kJ/mol on Ni(111). In contrast, the heats of formation of these three species on Pt (111) of −168 kJ/mol for methoxy,[11] −99 kJ/mol for O_{ad},[39] and −50. kJ/mol for methyl[40] give an endothermic enthalpy for reaction 2 of +19 kJ/mol. Clearly, such simple C–O bond-cleavage reactions that produce O adatoms are much more exothermic (by almost 100 kJ/mol) on Ni than Pt catalysts, and thus should be much faster and have much larger equilibrium constants on Ni catalysts. Similarly, C–O bond forming reactions (like the reverse of reaction 2) should be much more facile on Pt than Ni catalysts. In contrast, C–O bond cleavage reactions that involve oxygen transfer to another surface fragment rather than to produce O_{ad} should be similar on Ni and Pt catalysts, as seen for the simple reaction:

$$CH_3O_{ad} + H_{ad} \rightarrow CH_{3,ad} + OH_{ad} \quad (3)$$

The enthalpy for reaction 3 is −69 kJ/mol on Ni(111) and quite similar, −54 kJ/mol, on Pt(111). (The heat of formation of H_{ad} is −47 kJ/mol on Ni(111)[22] and −36 kJ/mol on Pt(111).[22] The heat of formation of OH_{ad} is −278 kJ/mol on Ni(111)[12] and −208 kJ/mol on Pt(111).[22,41])

Trends in Bond Enthalpies of Adsorbed Oxygenates. It has previously been shown that the ligand–metal σ-bond strengths found in organometallic complexes in liquid solutions strongly correlate with the corresponding gas-phase ligand–hydrogen bond strength.[42−44] Previously this research group found that this trend is also true for ligands (i.e., molecular fragments) bound to Pt(111).[14] Specifically, the adiabatic bond dissociation enthalpies of oxygenate adsorbates to Pt(111) (monodentate formate, hydroxyl, and methoxy) vary linearly with a slope of 1 with the corresponding gas-phase RO–H σ bond enthalpy but offset by −251 kJ/mol. Analyzing the bond enthalpy of methoxy measured in this work and the bond enthalpies of formate and hydroxyl measured previously[12,13] on Ni(111), we find this same trend, as shown in Figure 5, which shows the adiabatic bond dissociation enthalpies of three oxygenate adsorbates, which we refer to here as "ligands" (or L), on both Ni(111) and Pt(111) versus their corresponding gas-phase hydrogen–ligand bond dissociation enthalpies. The data points and trendline for Pt(111) are recreated here from the literature[14] and adjusted slightly to account for systematic error equal to RT_{source}, as discussed

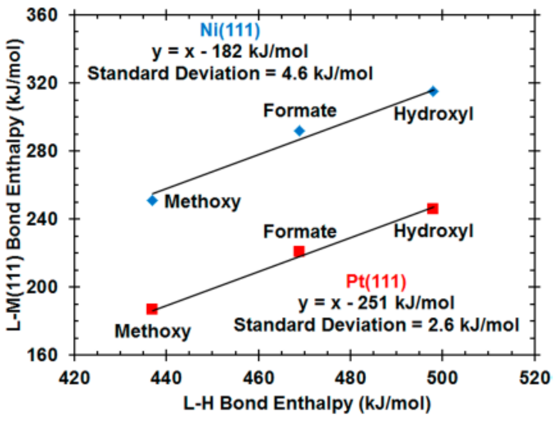


Figure 5. Calorimetric bond dissociation enthalpies of three adsorbates (i.e., ligands, L) on both Ni(111) and Pt(111) versus their corresponding gas-phase hydrogen–ligand bond dissociation enthalpies. These data points are fitted with the linear trendlines shown, each with a slope of 1.

elsewhere.[22] A linear trend with a slope of 1 ($y = x - 182$ kJ/mol) is shown on Figure 5 to fit the data points for Ni(111) very well and possesses a standard deviation of 4.7 kJ/mol. The best-fit line of variable slope ($y = 1.05x - 207$ kJ/mol) fits only slightly better, with a standard deviation of 4.6 kJ/mol. The strength of σ-bonds of adsorbed oxygen-bound molecular fragments to Ni(111) varies linearly with the strength of binding of those same fragments to H atoms in gas-phase molecules with a slope of 1.00, but offset by −182 kJ/mol. It is weaker than binding to a H atom, but ~69 kJ/mol stronger than binding to Pt(111), which makes sense because Ni is known to be more oxophillic than Pt. Therefore, we are able to predict the bond enthalpies of other oxygen-bound molecular framents to Ni or Pt through these trend lines. This will probably fail for larger adsorbates, because these will have strong van der Waals attractions to the surface as well, which are not accounted for in the trends in Figure 5. Given that these trends of Figure 5 hold for both Pt(111) and Ni(111), we expect that the bond enthalpies of small adsorbed oxygenates to other transition metal surfaces will follow a similar trend with a slope near 1.

CONCLUSIONS

The energetics of the molecular and dissociative adsorption of methanol on Ni(111) were measured by SCAC. At 100 K, the heat of adsorption is well fit by the curve ($63.2-23.9\ \theta$) kJ/mol from 0−0.30 ML and ($99.3-142.7\ \theta$) kJ/mol from 0.30−0.40 ML. The dissociative adsorption of methanol on O-precovered Ni(111) produces adsorbed methoxy and hydroxyl and gives an integral heat of adsorption at 155 K of −70. kJ/mol at a coverage of 0.25 ML (of both products). This gives a heat of formation for adsorbed methoxy of −233 kJ/mol and a bond enthalpy of 250. kJ/mol. We find a linear trend with a slope of 1 between the bond enthalpies of small oxygenates to Ni(111) and Pt(111) and their corresponding gas-phase hydrogen−ligand bond dissociation enthalpies. These values and trends improve our ability to understand the selectivity, reaction rate, and activity differences between metal surfaces in reactions involving adsorbed oxygenates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b02992.

> Sticking probabilities and heats of adsorption of methanol on Ni(111) versus coverage for different surface temperatures and oxygen precoverages (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge support for this work by the National Science Foundation under Grant no. CHE-1665077. We would like to thank Gregory Arps for his assistance in the laboratory.

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DOI: 10.1021/acscatal.8b02992
ACS Catal. 2018, 8, 10089–10095