

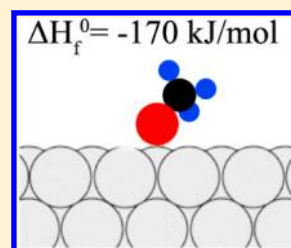
Energetics of Adsorbed Methanol and Methoxy on Pt(111) by Microcalorimetry

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ABSTRACT: The heat of adsorption and sticking probability of methanol were measured on clean Pt(111) at 100, 150, and 210 K and on oxygen-precovered Pt(111) at 150 K by single-crystal adsorption calorimetry (SCAC). On clean Pt(111) at 100 K, the heat of methanol adsorption was found to be 60.5 ± 0.8 kJ/mol in the limit of low coverage, resulting in a standard enthalpy of formation (ΔH_f°) of $\text{CH}_3\text{OH}(\text{ad})$ of -263 ± 0.8 kJ/mol. The results at 150 and 210 K on clean Pt(111) were indistinguishable from the energetics measured at 100 K in the same coverage range. Calorimetry of methanol on oxygen-precovered Pt(111) at 150 K yielded the energetics of adsorbed methoxy, giving $\Delta H_f^\circ[\text{CH}_3\text{O}(\text{ad})] = -170 \pm 10$ kJ/mol and a $\text{CH}_3\text{O}-\text{Pt}(111)$ bond enthalpy of 187 ± 11 kJ/mol. By use of these enthalpies, the dissociation of adsorbed methanol on Pt(111) to form methoxy and a hydrogen adatom is found to be uphill by $+57$ kJ/mol. At coverages below 0.2 monolayer (ML), the sticking probability for methanol on both surfaces at or below 150 K was >0.95 . At 210 K, $\sim 80\%$ of the methanol beam pulse transiently adsorbs to clean Pt(111) with a surface residence time of 238 ms and heat of adsorption of 61.2 ± 2.0 kJ/mol, giving a prefactor for methanol desorption of $4 \times 10^{15 \pm 0.5} \text{ s}^{-1}$. These measured energetics for methoxy and methanol were compared to density functional theory (DFT) calculations from previous literature, showing DFT to routinely underestimate the bond energy of both adsorbed methanol and methoxy by 15–52 kJ/mol.



INTRODUCTION

The catalytic reforming and decomposition of oxygenates has attracted much attention for the production of high-purity hydrogen and for applications in direct alcohol fuel cells. The transition metals Pt, Rh, Ni, and Pd are typical catalysts used to facilitate these reactions, with Pt being a very active metal. Methanol is an appealing oxygenate for these reactions because it has a high H/C ratio; lacks a C–C bond, allowing good selectivity at lower temperatures; and is a liquid under standard conditions that can be easily transported. As such, much work has been dedicated to elucidating the chemical pathway methanol follows on Pt surfaces. Microkinetic models have been developed^{1,2} in which many intermediates have been proposed, but only a few have been directly observed. One of the more stable intermediates in these pathways is surface-bound methoxy, which has been observed under reaction conditions on Pt-supported catalysts^{3–6} and in ultrahigh vacuum (UHV) conditions on Pt single-crystal surfaces^{7–11} and thus because of its stability is thought to play an important role in the rate-limiting steps of these reactions. Adsorbed alkoxy species, of which methoxy is the simplest, are also ubiquitous intermediates in many catalytic combustion, selective oxidation and steam re-forming reactions that take place on Pt and/or Pt group metals.

Since the important catalytic parameters of selectivity and activity depend on the thermodynamic stability of adsorbed intermediates, it is important that the energetics (heat of adsorption, bond strength, etc.) of methoxy be measured. Typically, such measurements are made on single-crystal surfaces, since only on such surfaces can well-defined adsorbed

intermediates be cleanly produced. On such surfaces, heats of adsorption are often measured by techniques like temperature-programmed desorption (TPD) and equilibrium adsorption isotherms. However, those techniques require the adsorbate to adsorb and desorb reversibly, which methoxy does not; instead, it decomposes upon heating. Therefore we employ the only technique available, single-crystal adsorption calorimetry (SCAC), to provide a direct measurement of the energetics of methoxy as a function of coverage on Pt(111).

There are two known ways to cleanly produce methoxy species on Pt(111) in UHV conditions. One method involves dosing methyl nitrite on Pt(111) at $\sim 165 \text{ K}^{10,11}$ to yield methoxy coadsorbed with NO, and the second requires dosing methanol on an oxygen-precovered Pt(111) surface at 150 K, producing methoxy coadsorbed with hydroxyl.^{7–9} In this work, we measured the energetics of adsorbed methoxy prepared by the latter method, because the energy of the coadsorbed hydroxyl can be accounted for by use of our previous SCAC measurements of adsorbed hydroxyl on Pt(111),^{12,13} allowing the energetics of adsorbed methoxy to be extracted. We also present SCAC results of methanol on clean Pt(111) at 100, 150, and 210 K to provide the energetics of molecularly adsorbed methanol and its surface residence time at 210 K, giving the prefactor for methanol desorption from the Pt(111) surface. Finally, we use our measured values to calculate heats of reaction for methanol dissociation on Pt(111) and compare the methoxy and methanol bond energies to density functional

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theory (DFT) calculations, providing benchmarks for its improvement.

■ EXPERIMENTAL SECTION

Experiments were performed in a UHV chamber (base pressure $<2 \times 10^{-10}$ mbar) equipped with X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low-energy ion scattering spectroscopy (LEIS), low-energy electron diffraction (LEED), and SCAC. The apparatus and procedures for SCAC have been described previously.^{14,15}

The sample used was a 1 μm thick Pt(111) single-crystal foil, supplied by Jacques Chevallier at Aarhus University in Denmark. The sample surface was cleaned by 1.25 kV Ar⁺ ion sputtering, annealing at 1123 K, then gentle heating at 773 K in 1×10^{-8} mbar O₂(g) for 1 min to remove any surface carbon, and finally flash heating to 1123 K (<1 s). After this treatment, impurities were below the detection limit of AES, and the surface gave a very sharp Pt(111) LEED pattern.

Before calorimetry, the clean Pt(111) sample was brought to thermal equilibrium with the calorimeter and then flash-heated to 1123 K (<1 s) to ensure a clean surface. The sample was then brought back into contact with the pyroelectric detector and thermal equilibrium was re-established (in about 5 min), after which the experiment was performed. Note that to produce the Pt(111) surface precovered with 0.25 monolayer (ML) of O adatoms [p(2 \times 2) overlayer] the surface was exposed to 1×10^{-7} mbar of O₂(g) for 60 s from a directed doser immediately after this heating, so that the sample was still above 150 K during dosing to dissociate all of the adsorbed O₂.

Calorimetry was performed by exposing the surface to a pulsed molecular beam of methanol (CH₃OH) gas. Each pulse was 102 ms long and was repeated every 2 s. The methanol (Alfa Aesar, anhydrous, 99.9%) was outgassed by several freeze–pump–thaw cycles after being put into its reservoir on the vacuum chamber. Its purity was checked with a mass spectrometer and found to be consistent with the manufacturer's claim. The beam was created by expanding ~ 1.3 mbar of methanol through a microchannel array at 299 ± 6 K (defining the gas temperature) and then collimated through a series of five liquid-nitrogen-cooled orifices as described previously.¹⁶ Coverages are reported in monolayers (ML) and are defined as the number of methanol molecules that adsorb to the surface irreversibly, normalized by the number of platinum surface atoms in the Pt(111) surface (1.50×10^{19} Pt atoms/m²). A typical methanol dose was ~ 0.01 ML (1.88×10^{12} molecules) per pulse with a beam spot size previously determined to be 4.36 mm in diameter.¹⁶ In a given run, the dose per pulse was highly precise ($<1\%$ pulse-to-pulse variation, determined by the reproducibility of the chopper's beam-open time). The absolute accuracy of the measurement of the number of molecules per pulse was better than the measured 3% accuracy of the combined heat measurement, but how much better is difficult to determine. A more detailed description of the experimental principles and implementation of the molecular beam can be found elsewhere.^{16,17} The flux of methanol from the molecular beam is measured by impinging the beam onto a liquid-nitrogen-cooled quartz crystal microbalance (QCM), precovered with multilayers of methanol. Calibration of the QCM has been described previously.¹⁶

The heat released from the adsorption of one methanol pulse is measured with a pyroelectric polymer ribbon gently pressed against the back side of the Pt(111) sample.^{14,18} The sensitivity of the pyroelectric detector was calibrated after each experiment by depositing a known amount of energy into the sample by use of a HeNe (632.8 nm) laser. The absolute accuracy of the calorimetric heats is estimated to be better than 3% (i.e., any systematic errors are less than 3%) for systems like those studied here, which have sticking probabilities above 0.8. This is based on comparisons to literature values for standard enthalpies of sublimation of the bulk solid when solids with known enthalpies are formed, specifically multilayers of adsorbed cyclohexene,¹⁷ methanol (this work), methyl iodide,¹⁹ and water¹⁵ on Pt(111). For these molecules, the differences between the measured value and the estimated heat of sublimation based on the literature values for the standard enthalpies of phase transition (after

correction for temperature differences using literature values for heat capacities) were -5.6% , -3.3% , $<1\%$, and -5.1% , respectively. Note these differences from bulk sublimation values may be due to errors in the literature values or the possibility that we were not producing exactly the most stable phase at these low temperatures (possibly explaining the fact that our heats are lower than the literature values in the two cases where they differ most). However, these differences are all within the error bars (at 95% confidence) of the two values being compared, and therefore they do not really differ in any statistically significant way. Relative measurements (for example, differences in heat with changes in coverage or temperature) can be much more accurate. The precision of energy calibration can be improved as much as desired by averaging multiple runs.

Sticking probabilities were measured simultaneously with calorimetric measurements, via the King and Wells method.²⁰ A mass spectrometer, without line-of-sight to the sample, measured the background pressure increase of methanol, CH₃OH(g) ($m/z = 31$) in the chamber. A gold flag was positioned in front of the sample and used to determine the mass spectrometry signal corresponding to full reflection of methanol. The gold flag was used because methanol does not stick to gold at room temperature.²¹ The sticking probability of methanol is calculated by integrating the mass spectrometer signal measured from the increase in methanol partial pressure above background when the molecular beam is pulsed onto the sample surface in comparison with the increase in methanol partial pressure resulting when pulsed onto the inert gold flag. We report two types of sticking probabilities, long-term and short-term.¹⁷ The long-term sticking probability, S_{∞} , is the probability that a gas molecule strikes the Pt(111) surface, sticks, and remains until the next gas pulse starts ~ 2 s later. This measurement is used to calculate the adsorbate coverage remaining at the start of the next gas pulse. The short-term sticking probability, $S_{140 \text{ ms}}$, is the probability that a gas molecule strikes the Pt(111) surface, sticks, and remains at least throughout the time frame of our heat measurement (i.e., the first 140 ms). This is used to calculate the moles of gas-phase reactant that contribute to the measured heat of adsorption, so we can report that value in kilojoules per mole adsorbed. When there is no desorption between pulses, the two sticking probabilities are the same.

The calorimeter and Pt(111) sample are cooled by a large thermal reservoir, but one cannot mount a thermocouple directly on the ultrathin single crystal used for calorimetry nor on the sample platen to which it is mounted (because this whole platen is removed from its manipulator and mounted on the thermal reservoir during calorimetry to achieve better signal stability). Therefore, the sample temperature was monitored by two alumel/chromel thermocouples spot-welded to the two closest locations, one spot-welded to the holder of the pyroelectric detector and another to the thermal reservoir. We took the average of these two temperature readings as the sample temperature here. For the sample temperatures used here (100–210 K), the readings of these two thermocouples differed by ~ 20 K on average.

■ RESULTS

Sticking Probability. As described previously¹⁷ and above, we measured two types of sticking probabilities: the long-term sticking probability, S_{∞} , and the short-term sticking probability, $S_{140 \text{ ms}}$. Figure 1 shows both of these sticking probabilities for methanol versus coverage on clean and oxygen-precovered Pt(111) at 100 and 150 K. Both start at 0.95 and approach unity in the coverage range 0–0.2 ML. The high sticking probability at low coverage indicates a precursor-mediated adsorption mechanism. This type of adsorption has also been observed for benzene,²² naphthalene,²³ cyclohexene,¹⁷ and water¹⁵ on Pt(111). The slight increase in sticking probability from 0.95 to 1 as the coverage increases in the first 0.2 ML may be due to temporary attachment of the mobile precursor to a previously adsorbed methanol molecule, which may prevent it from desorbing before it can reorient and achieve the more

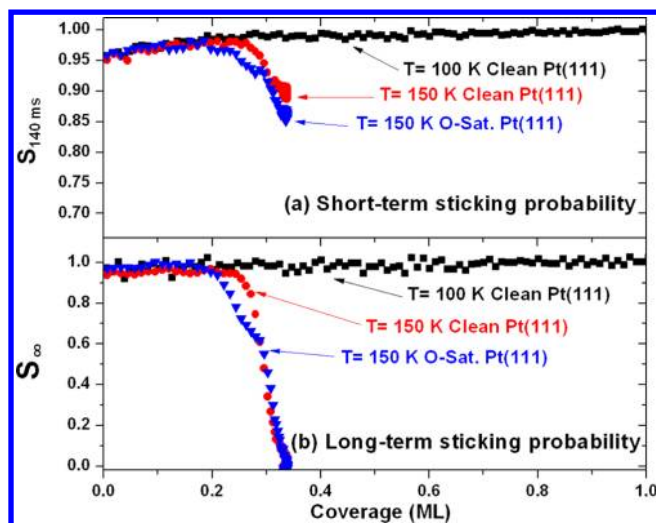


Figure 1. Average (a) short-term and (b) long-term sticking probability of methanol versus total methanol coverage: (squares) on clean Pt(111) at 100 K, (circles) on clean Pt(111) at 150 K, and (triangles) on oxygen-precovered Pt(111) at 150 K.

stable bonding structure required to keep it permanently on the Pt. After 0.2 ML, the sticking probabilities for the different surfaces and temperatures diverge.

For the clean Pt(111) surface at 100 K, the sticking probability is near unity for all coverages, in agreement with the observations of Akhter and White.⁹ At these conditions, methanol adsorbs molecularly in the first layer through its oxygen atom to atop sites^{7,24} and at higher coverages forms an amorphous multilayer.²⁴ Previous TPD experiments have observed this multilayer to desorb at ~ 140 K,⁷ and therefore, a multilayer is not expected to form when methanol is dosed on a clean Pt(111) surface at 150 K. Figure 1 confirms that a multilayer does not form on a clean Pt(111) surface at 150 K and instead a saturation coverage of 0.33 ML is reached. The third experiment shown in Figure 1 is the sticking probability of methanol on a Pt(111) surface at 150 K precovered with 0.25 ML of oxygen adatoms. When methanol is dosed onto this surface, adsorbed oxygen acts as a Lewis base to abstract a hydrogen from the adsorbed methanol, leaving methoxy and hydroxyl adsorbates on the surface.^{7–9} Even though this surface reaction is occurring, the same saturation coverage of 0.33 ML is obtained as for the clean Pt(111) surface at 150 K. Note that the coverage axes in Figures 1–4 are, in all cases, the total coverage of methanol that stuck to the surface (measured as the long-term sticking probability multiplied by the beam flux and pulse duration), irrespective of the final products it produced. The observed total surface coverage of 0.33 ML is in good agreement with the saturation coverage of 0.36 ML for methanol on the oxygen-precovered surface reported by Akhter and White.⁹

The sticking probability versus coverage for methanol on clean Pt(111) at 210 K is shown in Figure 2. Since TPD experiments have shown that the first layer of methanol desorbs from Pt(111) at 180 K, methanol is not expected to adsorb on a clean Pt(111) surface at 210 K. The results of Figure 2 confirm this, showing that the saturation coverage is only 0.008 ML, which builds up in the first few pulses and might be associated with adsorption of methanol on defect sites. In contrast, the short-term sticking probability remains high (~ 0.8) after

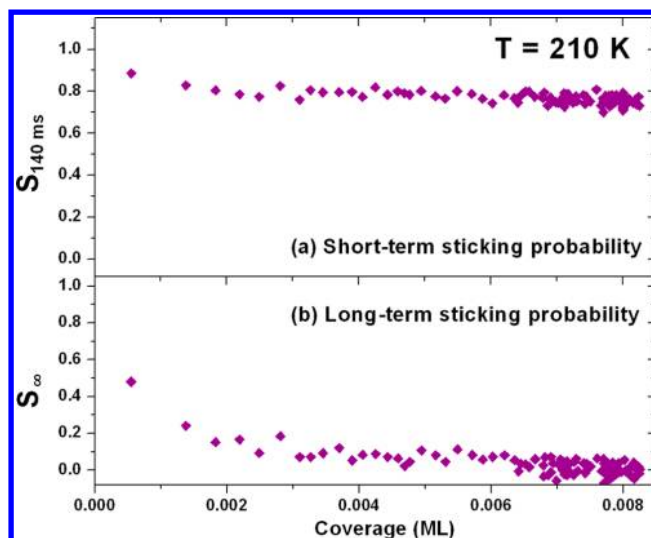


Figure 2. Average (a) short-term and (b) long-term sticking probability of methanol gas pulses versus total methanol coverage on clean Pt(111) at 210 K. Here the short-term sticking indicates that approximately 80% of the gas pulse sticks to the surface during the time scale of our heat measurement (140 ms). At times longer than 140 ms, all of the methanol desorbs at coverages above 0.008, as seen in the long-term sticking probability of 0.0.

hundreds of pulses, proving that $\sim 80\%$ of the molecules stick initially but desorb again before the next pulse.

Heat of Adsorption at 100 K on Clean Pt(111). In this paper we define the term *heat of adsorption* as the negative of the differential standard molar enthalpy change for the adsorption reaction, with the gas and the Pt(111) surface being at the same temperature. During our experiments, the temperature of the molecular beam is ~ 300 K, while the Pt(111) sample is held at cryogenic temperatures (e.g., 100 K). Thus, the measured heat is corrected by the small difference in the internal energy of the gas in the *directed* molecular beam at 300 K and in a Boltzmann distribution at the sample temperature, and then by RT to convert from internal energy change to enthalpy change for the adsorption reaction, as described elsewhere.¹⁷

The heat of adsorption of methanol on clean Pt(111) at 100 K is shown in Figure 3. Initially, methanol adsorbs molecularly through its oxygen atom with a heat of adsorption of 60.5 ± 0.8 kJ/mol in the limit of low coverage. As coverage increases to 0.5 ML, the heat of adsorption decreases, which is not surprising since TPD has shown the first layer peak desorption temperature to decrease with increasing coverage.²⁵ For the first $1/3$ ML, the heat of adsorption is well described by a best-fit line $(60.5 - 19.3\theta)$ kJ/mol, where θ is coverage, in monolayers, yielding an average heat of 57.3 kJ/mol.

Insight into the nature of the repulsive adsorbate–adsorbate interactions that give rise to this decreasing heat can be obtained by estimating the footprint of an adsorbed methanol from the van der Waals radius of methane (1.70 Å),²⁶ giving a diameter of adsorbed methanol of ~ 3.4 Å. Since this is much smaller than the next nearest neighbor Pt–Pt distance (4.8 Å),²⁷ the decrease in adsorption energy up to $1/3$ ML coverage is probably due to dipole–dipole repulsions. However, the distance between nearest-neighbor sites (2.77 Å)²⁷ is less than the footprint of methanol (3.4 Å), so there will be stronger steric repulsions at nearest-neighbor sites. Thus, it is likely that methanol saturates next nearest neighbor sites first, to avoid

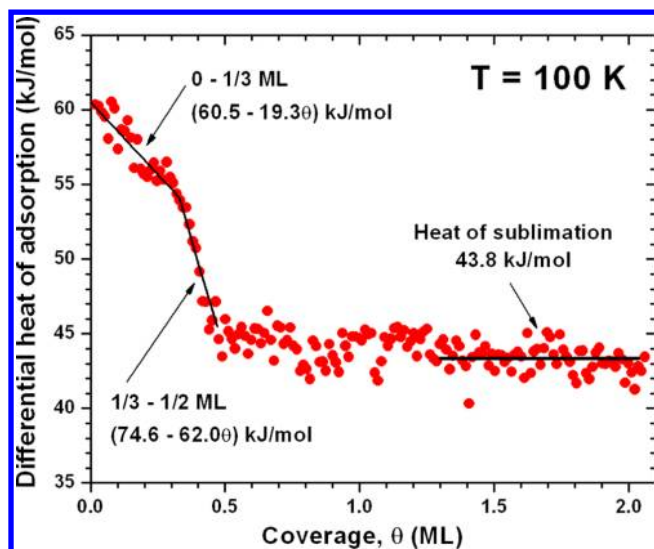


Figure 3. Differential heat of adsorption of methanol on clean Pt(111) at 100 K versus total methanol coverage. Each data point represents a pulse of 0.01 ML of methanol gas and is a result of averaging 10 experimental runs.

these steric repulsions, forming a local $(\sqrt{3} \times \sqrt{3})$ structure at $1/3$ ML.

Following Persson's model,²⁸ this linear decrease in adsorption energy in the first $1/3$ ML can be explained by immobile adsorbates that randomly populate next nearest neighbor sites (but not closer) with repulsive interactions between adsorbates at next nearest neighbor sites (but not further) and no relaxation of this repulsion by slight movement apart for an isolated pair (i.e., Persson's $\epsilon = 0$). When Persson's model is adapted to a hexagonal lattice, the initial heat of adsorption (60.5 kJ/mol) is the heat of adsorption for a single isolated adsorbate (Persson's μ) and the slope (-19.3 kJ \cdot mol $^{-1}\cdot$ ML $^{-1}$) is equal to $-6V_0$ per $1/3$ ML, where V_0 is the pairwise repulsion between adsorbates at next nearest neighbor sites (1.1 kJ/mol here).

This decrease in heat below 0.33 ML could be the result of a much more complex situation than the simple model above, as suggested by recent scanning tunneling microscopy (STM) and DFT studies of methanol on Cu(111) and Au(111).^{29,30} On both surfaces, the methanol molecules lie sideways on the surface and cluster together into hydrogen-bonded hexamers and/or chains, with the methyl groups pointing outward. Chains are formed at 145 K on Cu(111), and there are repulsive interactions between the chains such that the saturation coverage is $1/3$ ML.³⁰ If the same chains and/or hexamers form here on Pt(111) already at 100 K, then this decrease in heat may be due to hexamer-hexamer or chain-chain repulsions, instead of the simple molecule-molecule repulsions suggested above.

After 0.33 ML and up to 0.5 ML, the heat of adsorption decreases much more rapidly and is well described by the best-fit line (74.6 – 62.0 θ) kJ/mol. The abrupt change in slope at 0.33 ML suggests that as the $(\sqrt{3} \times \sqrt{3})$ structure completes, methanol continues to adsorb but now must populate nearest-neighbor sites, completing a $c(2 \times 2)$ structure at $1/2$ ML. The stronger steric repulsions between adsorbates at nearest-neighbor sites explain this more rapid decrease in adsorption energy. The integral heat of adsorption at 0.5 ML is 54.2 ± 0.8 kJ/mol from Figure 3. This can be compared to heats of

adsorption of 47 kJ/mol⁸ and 48 kJ/mol²⁵ reported for the saturated first layer based on TPD. (For comparison to heats of adsorption, we added $1/2RT$ here to the reported desorption activation energies, as described elsewhere.³¹) These heats are 7–8 kJ/mol lower than our measured integral heat of adsorption, a discrepancy that is due to the assumption of 10^{13} s $^{-1}$ as the desorption prefactor in refs 8 and 25 to extract desorption energies. We show below that this prefactor is instead $4 \times 10^{15 \pm 0.5}$ s $^{-1}$, which would increase these enthalpies by ~ 9 kJ/mol and bring the values within ~ 1 – 2 kJ/mol.

At coverages greater than 0.5 ML, the heat of adsorption becomes nearly constant, implying that additional methanol adsorbs on top of methanol adsorbates, growing as a multilayer above 0.5 ML at 100 K. Above 0.8 ML, the multilayer adsorption energy is 43.8 ± 0.8 kJ/mol. This value is in excellent agreement with the heat of sublimation of bulk methanol (solid) at 100 K, 45.3 kJ/mol, calculated from bulk thermodynamic data,^{32–34} and 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/mol³⁵ (after correction using bulk solid and gas-phase heat capacities from 150 K down to 100 K).

Heat of Adsorption at 150 K on Clean and Oxygen-Precovered Pt(111). Figure 4 displays heat of adsorption

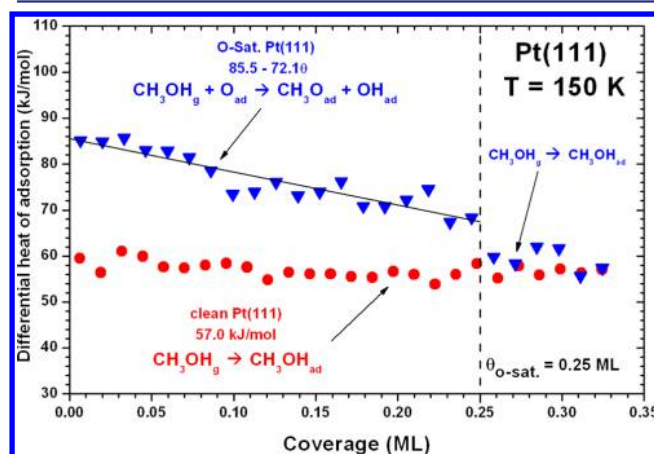


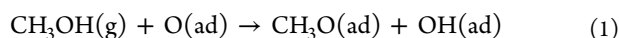
Figure 4. Differential heat of adsorption of methanol versus total methanol coverage on (circles) clean and (triangles) oxygen-saturated Pt(111) at 150 K. On the oxygen-saturated surface, methanol reacts to form adsorbed methoxy and hydroxyl species, giving an average heat of reaction of 76.4 kJ/mol. This reaction takes place only when adsorbed oxygen is still present, which is only up to a coverage of 0.25 ML (or to the dashed line, which indicates the total amount of O(ad) preadsorbed to the surface.) On clean Pt(111), methanol adsorbs molecularly, giving an average heat of 57.0 kJ/mol.

versus coverage for two experiments at 150 K: one where methanol is dosed on clean Pt(111), and a second where methanol is dosed on a Pt(111) surface at 150 K that had been preadsorbed with 0.25 ML of oxygen adatoms.

At 150 K on clean Pt(111), methanol does not form a multilayer and is known to adsorb molecularly through its oxygen atom at atop sites.⁷ Figure 4 shows that the heat of adsorption of methanol on Pt(111) at 150 K is relatively constant, giving an average heat of adsorption of 57.0 kJ/mol in the coverage range 0–0.33 ML, which is statistically identical (i.e., within the 95% confidence interval) to the average heat of adsorption of 57.3 kJ/mol in the same coverage range measured at 100 K (Figure 3). Note the maximum coverage is 0.33 ML at

150 K, meaning only the $(\sqrt{3} \times \sqrt{3})$ -like structure is formed, with methanol in next nearest neighbor sites. Any coverage greater than 0.33 ML would require methanol to adsorb in nearest-neighbor sites with strong steric repulsions, which is a structure too unstable to form at this temperature.

Next, we studied the heat of methanol adsorption on the Pt(111) surface predosed with oxygen adatoms under conditions where it is known to produce adsorbed methoxy and hydroxyl species. Previous TPD^{7–9} and high-resolution electron energy loss spectroscopy (HREELS)^{7,8} studies have shown that predosed oxygen adatoms on the Pt(111) surface, at O(ad) coverages up to 0.25 ML, abstract a hydrogen atom from adsorbed methanol to form adsorbed methoxy and hydroxyl species above 140 K (eq 1):



At temperatures greater than 150 K, the methoxy adsorbates become unstable and decompose, ultimately evolving $\text{H}_2(\text{g})$, $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$, and $\text{H}_2\text{O}(\text{g})$ in TPD experiments.⁹ In SCAC experiments, it is best to choose a temperature where the reaction of interest occurs as fast as possible, to avoid complications in heat signal analysis from slow heat deposition due to slow kinetics of the surface reactions, H abstraction here.¹⁵ Thus, experiments are done at the highest temperature where the reaction occurs cleanly. Therefore, methanol was dosed on the oxygen-predosed Pt(111) surface at 150 K, which is the maximum temperature at which methoxy and hydroxyl species are formed without further decomposition of the adsorbed methoxy.⁹ The oxygen adatoms were predosed by use of an exposure of $\sim 1 \times 10^{-7}$ mbar of $\text{O}_2(\text{g})$ for 60 s to the clean Pt(111) surface at 150 K, which is known to produce saturation coverage of 0.25 ML of oxygen adatoms in a $p(2 \times 2)$ structure.^{36–38} During this experiment, no broadening in the heat signal line shape was observed, indicating that the kinetics of the reaction are indeed fast within the time frame of our heat measurement.

The results of this experiment (Figure 4) show the heat of adsorption is approximately 19 kJ/mol higher than on the clean Pt(111) surface. The higher heat, associated with the methanol reacting to form methoxy and hydroxyl adsorbates, is only apparent in the coverage range 0–0.25 ML. Above 0.25 ML, the heat of adsorption is almost identical on the clean and O-predosed Pt surfaces: 56.8 and 58.9 kJ/mol, respectively. This is consistent with the reaction stoichiometry [one methanol reacts per O(ad)] and the oxygen precoverage of 0.25 ML. Any additional coverage of methanol greater than 0.25 ML simply adsorbs molecularly. In the coverage region from 0 to 0.25 ML on the O-predosed surface, where methoxy and hydroxyl species are being produced, the heat of adsorption is well fit by the straight line $(85.5 - 72.1\theta)$ kJ/mol. The integral heat of adsorption at 0.25 ML is 76.4 kJ/mol.

Heat and Surface Residence Time of Transiently Adsorbed Methanol on Clean Pt(111) at 210 K. The sticking probabilities for methanol dosed onto Pt(111) at 210 K (Figure 2) show that $\sim 80\%$ of a pulse of methanol adsorbs transiently during the time frame of our heat measurement and then desorbs shortly thereafter, and this occurs repeatedly for many pulses. While no permanent accumulation of methanol occurs, the 80% that does stick during our heat measurement allows us to measure a heat of adsorption of 61.2 ± 2.0 kJ/mol, a value that is within the error bar of the zero-coverage limit of methanol adsorption on clean Pt(111) measured at 100 K, 60.5 ± 0.8 kJ/mol (Figure 3). If we take this measured heat of

adsorption at 210 K and assume nonactivated adsorption, the activation energy for desorption at this temperature is 60.3 kJ/mol (subtracting $1/2RT$ from the heat of adsorption, where T is the temperature of the sample).³¹

Figure 5 displays the line shape of the methanol signal (m/z 31) measured with our mass spectrometer for a single pulse

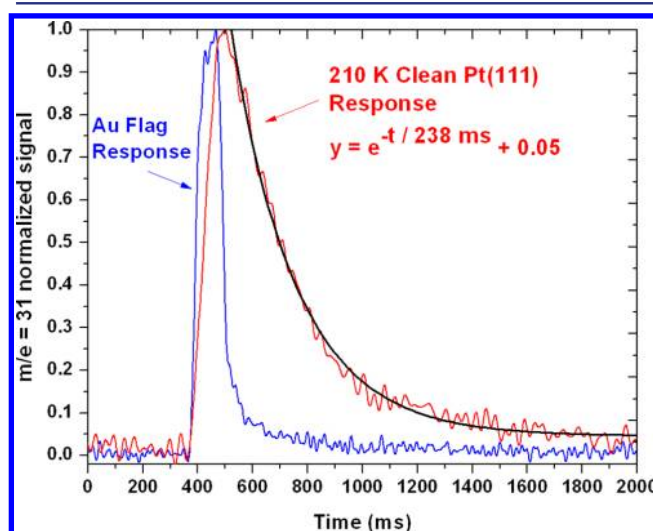


Figure 5. Normalized mass spectrometer signal versus time during the 2000 ms pulse cycle of methanol gas impinging on a Pt(111) surface held at 210 K, averaged over the first 30 pulses at the lowest coverage. The 100 ms pulse strikes the surface from ~ 380 to 480 ms on this scale. The slow desorption of methanol from the Pt(111) surface is apparent in the broad tail of the mass spectrometer response after this (red trace), which is fitted to an exponential decay with a 238 ms time constant (smooth black curve). For reference, the signal from the same 100 ms pulses of methanol after impinging on a room-temperature Au flag, where the molecules desorb rapidly, is also shown (blue trace).

period of methanol gas on the Pt(111) surface at 210 K, averaged over 30 pulses. For reference, the mass spectrometer signal of a pulse of methanol gas impinging on an Au flag, where methanol desorbs very rapidly, is also shown. The long tail seen in the line shape for methanol desorption from the 210 K Pt(111) surface is well fit with an exponential decay function of the form $y = e^{-t/\tau}$, representing first-order kinetics of the desorption process, giving $\tau = 238$ ms. Here τ represents the average surface residence time, which is equal to $1/k_{\text{des}}$, where k_{des} is the rate constant of methanol desorption from Pt(111). This $\tau = 238$ ms gives $k_{\text{des}} = 4.2 \text{ s}^{-1}$. Using the Arrhenius equation for k_{des} in conjunction with the desorption activation energy of 60.3 kJ/mol from the measured heat gives a pre-exponential factor for methanol desorption from Pt(111) of $4 \times 10^{15 \pm 0.5} \text{ s}^{-1}$.

DISCUSSION

Energetics of Adsorbed Methoxy on Pt(111). For the experiment of methanol dosed onto oxygen-precovered Pt(111) at 150 K, we attribute the integral heat of adsorption of 76.4 kJ/mol in the coverage range 0–0.25 ML (Figure 4) to the heat of reaction in eq 1. By use of this measured enthalpy of reaction (eq 1) at 150 K (-76.4 kJ/mol), a thermodynamic cycle is constructed to extract the standard heat (enthalpy) of formation (ΔH_f°) of adsorbed methoxy and the $\text{CH}_3\text{O}-\text{Pt}(111)$ bond enthalpy at 0.25 ML of coverage (Figure 6). (“Standard” here simply refers to 1 bar pressure.) The enthalpy

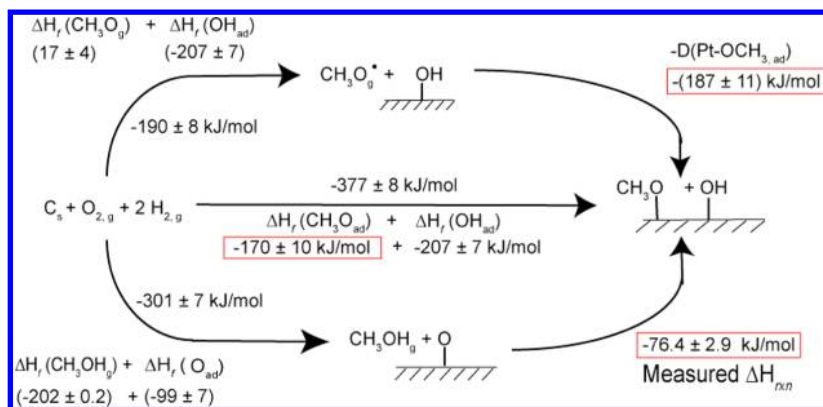


Figure 6. Thermodynamic cycle at 150 K used in calculating the bond enthalpy and standard heat of formation of adsorbed methoxy. Here -76.4 kJ/mol is the measured enthalpy of the reaction $\text{CH}_3\text{OH}(\text{g}) + \text{O}(\text{ad}) \rightarrow \text{OCH}_3(\text{ad}) + \text{OH}(\text{ad})$, from the data shown in Figure 4, integrated over the coverage range up to 0.25 ML of each product [corresponding to a starting coverage of 0.25 ML of $\text{O}(\text{ad})$]. The calculations from this cycle give a standard heat of formation for adsorbed methoxy [$\text{OCH}_3(\text{ad})$] on Pt(111) at 150 K of -170 ± 10 kJ/mol and a Pt–O bond enthalpy of 187 ± 11 kJ/mol for methoxy to the Pt(111) surface, both for a coverage of 0.25 ML of $\text{OCH}_3(\text{ad})$ coadsorbed with 0.25 ML of $\text{OH}(\text{ad})$.

of formation of adsorbed methoxy is found by first starting on the left-hand side of the cycle with the elements in their standard states and following the pathway of the bottom half of the cycle. The enthalpy for the lower left-hand step is found by adding the known enthalpy of formation of gas-phase methanol³⁹ with the known enthalpy of formation of adsorbed oxygen on Pt(111) at a coverage of 0.25 ML.¹³ The lower right-hand step is the measured integral enthalpy of reaction (eq 1), -76.4 kJ/mol from Figure 4. By adding the energies of the lower left- and right-hand steps, a total value of -377 ± 8 kJ/mol is found. This is the total enthalpy change in taking the elements in their standard states to methoxy coadsorbed with hydroxyl (both at 0.25 ML coverage), and therefore is equal to the sum of the enthalpy of formation of adsorbed hydroxyl and the enthalpy of formation of adsorbed methoxy. The standard enthalpy of formation of adsorbed hydroxyl on Pt(111) is known: $\Delta H_f^\circ[\text{OH}(\text{ad})] = -207 \pm 7$ kJ/mol.¹³ This reported value is for $\text{OH}(\text{ad})$ coadsorbed with H_2O in a very stable ($\text{H}_2\text{O}-\text{OH}(\text{ad})$) adlayer, where the $\text{OH}(\text{ad})$ was estimated to be 38 kJ/mol more stable than isolated $\text{OH}(\text{ad})$ on Pt(111) due to hydrogen bonding. We use this value [rather than that for isolated $\text{OH}(\text{ad})$] since we assume that hydrogen bonding will stabilize the $\text{OH}(\text{ad})$ coadsorbed with $\text{CH}_3\text{O}(\text{ad})$ to a similar magnitude. Subtracting this enthalpy of formation of adsorbed hydroxyl from -377 ± 8 kJ/mol results in the enthalpy of formation of adsorbed methoxy: -170 ± 10 kJ/mol.

By following the pathway depicted in the upper part of this thermodynamic cycle (Figure 6), the bond enthalpy of methoxy can be extracted. This is accomplished by again starting on the left-hand side of the cycle with the elements in their standard states, but now following the upper left-hand step that takes the elements in their standard states to gas-phase methoxy radical and adsorbed hydroxyl. The enthalpy for this step is determined by adding the known enthalpies of formation of gas-phase methoxy (17 ± 4 kJ/mol)⁴⁰ and adsorbed hydroxyl (-207 ± 7 kJ/mol),¹³ giving an enthalpy for this step of -190 ± 8 kJ/mol. The next step in the upper pathway is the adsorption of gas-phase methoxy onto the hydroxylated Pt(111) surface, depicted in the upper right-hand side of the cycle in Figure 6. The enthalpy for this step is found by summing the rest of the steps in the cycle, giving -187 ± 11 kJ/mol. Thus, the $\text{CH}_3\text{O}-\text{Pt}(111)$ bond enthalpy of methoxy

on Pt(111) is 187 ± 11 kJ/mol at 0.25 ML of methoxy coverage (coadsorbed with 0.25 ML of OH), based on our heat measurements in Figure 4 and other known thermodynamic data.

These methoxy species are coadsorbed with an equal amount of hydroxyl on the Pt(111) surface. In this situation, the adsorbates are expected to form hydrogen bonds that stabilize the overall structure. We compensated for this as described above with our choice of enthalpy of formation for $\text{OH}(\text{ad})$. Since this may overestimate the magnitude of this stabilization, we also performed the same cycle using the estimated enthalpy of formation of isolated $\text{OH}(\text{ad})$ on Pt(111), -169 kJ/mol.¹³ This results in a 38 kJ/mol stabilization in both the standard enthalpy of formation of adsorbed methoxy and the $\text{CH}_3\text{O}-\text{Pt}(111)$ bond enthalpy compared to the values in Figure 6. The real situation is somewhere between these two limits, probably closer to the values in Figure 6.

Comparisons to DFT Calculations and Evaluation of Enthalpy for Methanol Dissociation on Pt(111). The bond strengths measured in this work provide benchmarks for comparison to theoretical calculations. Table 1 compares computational values obtained by various DFT methods and

Table 1. Comparison of Present Calorimetric Bond Energies of Methanol and Methoxy to Pt(111) with DFT Values^a

coverage, ML	bond energy (kJ/mol)	
	exptl	DFT (functional and ref)
Methanol		
$1/_{37}$	59.4 ± 0.8	24 (PBE ⁴⁵), 49 (PBE-D2 ⁴⁵)
$1/_{16}$	$59. \pm 0.8$	72.4 (PBE ⁴⁶)
$1/_{9}$	58.6 ± 0.8	31.8 (PW-91 ^{41,42}), 20 (PW-91 ⁴³)
$1/_{4}$	57.3 ± 0.8	43.2 (PW-91 ⁴⁴)
Methoxy		
$1/_{16}$	186 ± 11^b	204 (PBE ⁴⁶)
$1/_{9}$	186 ± 11^b	149 (PW-91 ^{41,42}), 134 (PW-91 ⁴³)
$1/_{4}$	186 ± 11^b	161 (PW-91 ⁴⁴)

^aPresent values are determined from the integral heats of adsorption at the stated coverages. DFT values were calculated with periodic boundary conditions. ^bThis experimental bond energy for methoxy from Figure 6 is from the integral heat of adsorption of Figure 4 for a coverage of $1/_{4}$ ML (coadsorbed with $1/_{4}$ ML OH).

periodic boundary conditions to the experimental values of this work, for methanol and methoxy on Pt(111). Since DFT calculations report integral bond energies of adsorbates at specific coverages, the best-fit line to the measured differential heats of methanol adsorption versus coverage from 0 to 0.33 ML at 100 K (Figure 3) is used to extract integral heats of adsorption at specific methanol coverages to compare to DFT calculations. These integral heats (enthalpies) are then converted to bond energies by changing sign and subtracting RT . Bond energies of methanol to Pt(111) of 32 kJ/mol^{41,42} and 20 kJ/mol⁴³ at $1/9$ ML of coverage were calculated by two different groups using the GGA-PW91 functional. These values are ~ 27 and ~ 39 kJ/mol weaker, respectively, than our measured bond energy of 59 kJ/mol at $1/9$ ML. A similar calculation was performed by Desai et al.,⁴⁴ also using the GGA-PW91 functional but at $1/4$ ML of methanol coverage. This group found a bond energy of 43 kJ/mol for molecularly adsorbed methanol, which is only ~ 14 kJ/mol weaker than the measured 57 kJ/mol at this coverage. The weaker bond strength found in these DFT studies than by calorimetry could be due to methanol clustering together and forming hydrogen-bonded hexamers and/or chains, similar to what has been observed on Cu(111)³⁰ and Au(111),²⁹ discussed above. This situation could occur even at low coverages during the first dose of methanol to the surface. It could also be that these differences are due to those DFT calculations not including the energy of van der Waals interactions between the adsorbate and the surface. In a recent DFT study by Blonski and Lopez,⁴⁵ a nearly isolated methanol molecule (i.e., $1/37$ ML) was calculated on Pt(111) to have a bond energy of 24 kJ/mol by use of the PBE functional, but when the PBE-D2 functional was used to account for van der Waals interactions, the total bond energy increased to 49 kJ/mol, much closer to the experimental value of 59 kJ/mol. A study of methanol on Pt(111) by Cahyanto et al.⁴⁶ that also used the PBE functional calculated a bond energy of 72.4 kJ/mol, nearly 50 kJ/mol higher than the value of 24 kJ/mol calculated by Blonski and Lopez for the same PBE functional.⁴⁵ The value by Cahyanto et al. is so much higher than all the other DFT studies that it suggests they may have had some error.

Table 1 also compares calculated DFT values for the bond energy of methoxy to Pt(111) with these calorimetric results. With one exception, all of these DFT values are considerably lower than the measured bond energy of 186 kJ/mol, obtained from the measured bond enthalpy of 187 kJ/mol at 0.25 ML, after subtraction of RT . Only the DFT study by Cahyanto et al.⁴⁶ overestimated the bond energy of methoxy, with a value of 204 kJ/mol. As noted above, that DFT study may have had some error, since its bond energy for methanol to Pt(111) was also so much larger than the other DFT studies, even when the same PBE functional was used. Note that our measured value for methoxy is only for $1/4$ ML of methoxy coadsorbed with $1/4$ ML of OH. At coverages below $1/4$ ML, there is also unreacted O(ad) remaining on the surface in the experiments of Figure 4, which complicates conversion of heats to bond energies, so none are reported here at lower coverages. However, Figure 4 shows that the differential heat of adsorption decreases by only 16 kJ/mol with coverage in the first $1/4$ ML, and the integral heat decreases by only 8 kJ/mol, so this bond energy is not expected to change much with coverage in this range.

The measured heats of formation of methanol and methoxy allow estimation of the following reaction enthalpy on Pt(111):



$$\Delta H_2^\circ = +57 \pm 10 \text{ kJ/mol} \quad (2)$$

This heat of reaction is calculated from the measured enthalpy of formation of methoxy of -170 ± 10 kJ/mol at 150 K (Figure 6), the known enthalpy of formation of H(ad) on Pt(111) of -36 kJ/mol,¹⁷ and the enthalpy of formation of molecularly adsorbed methanol on Pt(111). For molecularly adsorbed methanol, the enthalpy of formation is found by adding the zero-coverage limit of the enthalpy of methanol adsorption on Pt(111) of -60.5 ± 0.8 kJ/mol from Figure 3 at 100 K (which was indistinguishable from measurements at 150 and 210 K) to the known enthalpy of formation of methanol gas of -202 ± 0.2 kJ/mol,³⁹ giving $\Delta H_f^\circ[\text{CH}_3\text{OH(ad)}] = -263 \pm 0.8$ kJ/mol. Note that the reaction in eq 2 is rather endothermic ($\Delta H_2^\circ = +57 \pm 10$ kJ/mol) and therefore should be very slow, perhaps even the rate-limiting step in catalytic reactions like methanol decomposition on Pt-based catalysts. The heat of reaction (eq 2) can also be compared to the DFT calculations of ref 41, which finds a nearly identical value of $+59$ kJ/mol. This excellent agreement suggests that comparing reaction energies to DFT calculations could be a more fair comparison than the bond energies listed in Table 1, since DFT may have errors associated with the gas-phase energies of methoxy and methanol.

CONCLUSIONS

At 100 K on clean Pt(111), methanol adsorbs molecularly through its oxygen atom at atop sites, forming a local ($\sqrt{3} \times \sqrt{3}$) structure with repulsive dipole–dipole interactions, resulting in a decreasing heat of adsorption that is well fit by $(60.5 - 19.3\theta)$ kJ/mol in the first $1/3$ ML of coverage. Above $1/3$ ML, the heat of adsorption drops much more rapidly until $1/2$ ML, probably corresponding to the population of a $c(2 \times 2)$ structure with strong steric repulsions between adsorbates. Above $1/2$ ML, methanol adsorbs with a nearly constant heat of adsorption, becoming equal to the multilayer sublimation enthalpy above 0.8 ML. At 150 K on clean Pt(111), only $1/3$ ML adsorbs, giving identical heats of adsorption as those measured at 100 K. These results provide the standard enthalpy of formation of adsorbed methanol, $\Delta H_f^\circ[\text{CH}_3\text{OH(ad)}] = -263 \pm 0.8$ kJ/mol, and the methanol–Pt(111) bond enthalpy of 60.5 ± 0.8 kJ/mol in the low-coverage limit. At 210 K on clean Pt(111), methanol adsorbs transiently with a surface residence time of 238 ms and a heat of ~ 61 kJ/mol, giving a prefactor for methanol desorption of $4 \times 10^{15 \pm 0.5} \text{ s}^{-1}$.

At 150 K, methanol reacts with a Pt(111) surface precovered with $1/4$ ML of oxygen adatoms to form adsorbed methoxy and hydroxyl in the first $1/4$ ML, giving an average enthalpy of reaction of -76.4 kJ/mol. Using known enthalpies of formation of gas-phase species, we find the standard enthalpy of formation of adsorbed methoxy to be $\Delta H_f^\circ[\text{CH}_3\text{O(ad)}] = -170 \pm 10$ kJ/mol and a CH₃O–Pt(111) bond enthalpy of 187 ± 11 kJ/mol.

The measured energetics for adsorbed methanol and methoxy on the Pt(111) surface were compared to DFT calculations from several different groups. These calculations consistently underestimated the bond strength of methanol and methoxy to the Pt(111) surface compared to measured values, in one case by 52 kJ/mol.

From these measured heats, the heat of reaction for the dissociation of adsorbed methanol to form H(ad) and methoxy on Pt(111) was found to be $+57 \pm 10$ kJ/mol.

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Notes

The authors declare no competing financial interest.

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