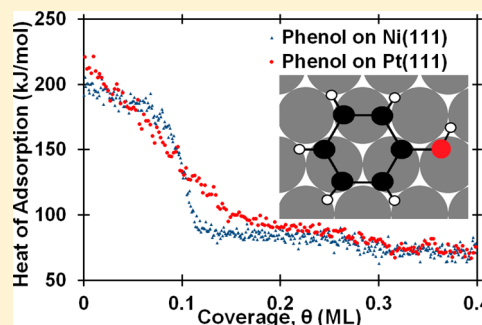


Energetics of Adsorbed Phenol on Ni(111) and Pt(111) by Calorimetry

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ABSTRACT: The heat of adsorption and sticking probability of phenol were measured on Ni(111) at 150 K and Pt(111) at 90 K using single crystal adsorption calorimetry (SCAC). Phenol adsorbs molecularly on both Ni(111) and Pt(111), with an initial heat adsorption of 200. kJ/mol on Ni(111) and 220 kJ/mol on Pt(111). The integral heat of adsorption at 1/9 ML coverage (-176 kJ/mol for Ni(111) and -175 kJ/mol for Pt(111)) gives a standard enthalpy of formation (ΔH_f^0) for $C_6H_5OH_{ad}$ of -272 kJ/mol on Ni(111) and -271 kJ/mol on Pt(111). The measured bonding energies for phenol to Ni(111) and Pt(111) were compared to density functional theory (DFT) calculations from previous literature, showing that DFT functionals that included van der Waals corrections are more accurate, although some calculations on both surfaces, even those with vdW corrections, still grossly underestimated the adsorption energy.



INTRODUCTION

Phenol is the simplest example of an aromatic oxygenate, a class of compounds that are involved in many important catalytic and electrocatalytic reactions on late transition metal surfaces. As such, it is often studied as a model compound to understand surface reactions for this class of compounds. For example, phenol is often used as a model for studying catalytic and electrocatalytic biomass conversion reactions over Pt, Ni, and other late transition metals.^{1–5} In order to better understand how phenol behaves in catalytic reactions, it is critical to know the energetics of phenol on catalyst surfaces. Here, we report the first calorimetric measurements of the adsorption energy of phenol on any transition metal surface, and extract from these the bond energies and heats of formation of phenol adsorbed on two model catalyst surfaces, Ni(111) and Pt(111). Phenol adsorption onto Ni(111) has been studied with temperature-programmed desorption (TPD), vibrational spectroscopy (RAIRS), and Auger electron spectroscopy (AES).⁶ These methods found that phenol chemisorbs molecularly parallel to the surface, interacting through its π -bonds with the surface. Multilayers of phenol already start desorbing at the lowest adsorption temperature studied (170 K). The first layer mainly decomposes during TPD, as evidenced by desorption peaks for H_2 (starting at ~ 300 K) and CO (starting at ~ 420 K).⁶ Phenol adsorption on Pt(111) has been studied with vibrational spectroscopy (HREELS),^{7–9} low-energy electron diffraction (LEED),⁸ AES,⁸ TPD,^{7,9} and X-ray photoelectron spectroscopy (XPS).⁹ Below 200 K, phenol adsorbs molecularly, parallel to the surface.^{7–9} At low temperatures, multilayers are formed that possess a desorption peak at 195 K. There is a transition (second) layer between the chemisorbed first layer and multilayers that interacts weakly with the Pt(111) surface. The adsorption energy of this layer is slightly stronger than the

multilayer, as evidenced by a TPD desorption peak at 225 K.⁹ At 200 K, adsorbed phenol dissociates by O–H bond scission, resulting in phenoxy and an adsorbed hydrogen atom.^{7,9} Further analysis shows that phenoxy transitions to a η^5 - π -adsorption or oxocyclohexadienyl species.⁹ By 490 K, this species decomposes to CO and H_2 gas, plus some carbon residue on the surface.⁹

EXPERIMENTAL SECTION

Experiments were performed in a UHV chamber (base pressure $< 2 \times 10^{-10}$ mbar) equipped with XPS, AES, low-energy ion scattering spectroscopy (LEIS), LEED, and SCAC. The sample used was a 1 μ m thick Ni(111) or Pt(111) single-crystal foil, supplied by Jacques Chevallier at Aarhus University in Denmark. The sample surface was cleaned by Ar^+ ion sputtering and annealing to remove contaminants. This treatment was repeated until impurities were below the detection limit of XPS, and the surface gave a very sharp LEED pattern. Detailed descriptions of the apparatus, molecular beam, sticking probability, heat measurements, and other procedures for SCAC may be found elsewhere.^{10–13}

Briefly, calorimetry was performed by holding the clean metal single crystal at a given temperature and exposing it to a pulsed molecular beam of phenol. The heat of adsorption was measured with a pyroelectric detector pressed against the backside of the sample.^{11,14} 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

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(632.8 nm) laser. The sticking probability was measured simultaneously with the heat of adsorption using a quadrupole mass spectrometer, as described previously.¹⁵ We report two types of sticking probabilities, long term and short term.¹² The long-term sticking probability, S_{∞} , is the probability that a gas molecule strikes the Ni(111) or Pt(111) surface, sticks, and remains until the next gas pulse starts ~ 3 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, $S_{102\text{ms}}$, is the probability that a gas molecule strikes the Ni(111) or Pt(111) surface, sticks, and remains at least throughout the time frame of our heat measurement (i.e., the first 102 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.

The molecular beam was created by expanding ~ 0.3 mbar of phenol (Sigma-Aldrich, >99%) through a microchannel array held at 300 ± 5 K (defining the gas temperature) and then collimated through a series of five liquid-nitrogen-cooled orifices. A chopper converts the beam into pulses that are 102 ms long and repeat every 3 s. Coverages are reported in monolayers (ML) and are defined as the number of phenol molecules that adsorb to the surface irreversibly, normalized by the number of metal surface atoms in the Ni(111) surface (1.86×10^{15} Ni atoms/cm²) or Pt(111) surface (1.50×10^{15} Pt atoms/cm²). A typical phenol dose was ~ 0.001 – 0.002 ML per pulse with a beam spot size previously determined to be 4.36 mm in diameter.¹⁰

RESULTS

Sticking Probability. As described previously¹² and above, we measured two types of sticking probabilities: the short-term sticking probability, $S_{102\text{ms}}$, and the long-term sticking probability, S_{∞} . Figure 1 shows the average short-term and

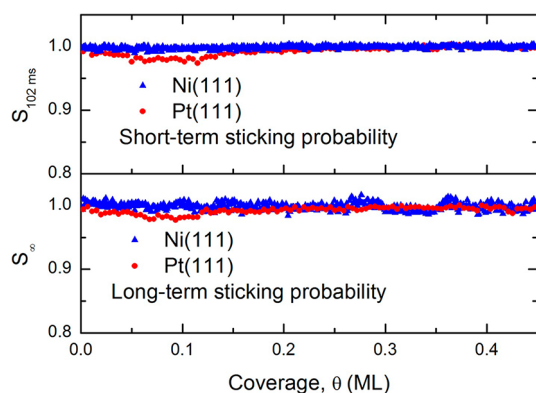


Figure 1. Average short-term and long-term sticking probabilities of phenol versus coverage at 90 K for Pt(111) and 150 K for Ni(111).

long-term sticking probabilities measured as a function of coverage on both Ni(111) and Pt(111). At these low temperatures, the sticking probability is near unity for both metal surfaces independent of coverage. On both surfaces, multilayer formation is expected and confirmed in this work.^{6,9} For Ni(111), both sticking probabilities start and remain very near unity for all experiments. For Pt(111), the initial short-term and long-term sticking probabilities start near unity but decrease slightly over the first 0.1 ML of coverage to ~ 0.98 and then increase to near unity at coverages above 0.15 ML after

the first layer saturates (see below). The lower sticking probability in the first layer on Pt(111) than in the multilayer or on Ni(111) may be due to poorer mass-matching in the gas-surface collision on Pt(111), as proposed for a similar observation for benzene on Pt(111).¹⁶ Poorer mass-matching in the gas-surface collisions results in a higher probability for quasi-elastic collisions and hence lower trapping probability.¹⁷

Heat of Adsorption of Molecular Phenol on Ni(111) at 150 K. In this paper, we define the term *heat of adsorption* as the negative of the differential standard molar enthalpy change for the adsorption reaction, ΔH_{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). During our experiments, the temperature of the molecular beam was ~ 300 K, while the Ni(111) sample was held at cryogenic temperatures (e.g., $T = 150$ K). Thus, the measured heat is corrected by the small difference in the internal energy of the gas in the *directed* molecular beam at its source temperature (300 K) and in a Boltzmann distribution at the sample temperature (T) and then by RT to convert from internal energy change to enthalpy change for the adsorption reaction, as described elsewhere.¹⁸

Figure 2 shows the heat of adsorption of phenol on the Ni(111) surface at 150 K. Under these conditions, phenol is

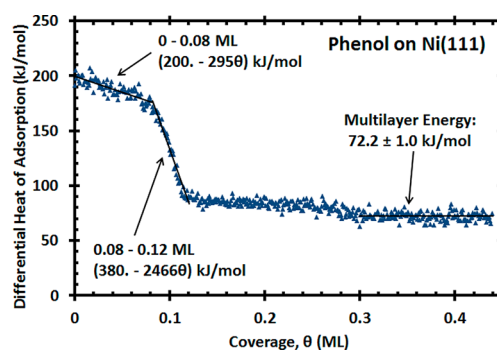


Figure 2. Differential heat of adsorption of molecularly adsorbing phenol on Ni(111) at 150 K as a function of adsorbed phenol coverage. Each data point represents a pulse of ~ 0.001 ML of phenol gas.

expected to adsorb molecularly, parallel to the surface.⁶ Phenol initially adsorbs with a heat of 200 kJ/mol. As the coverage increases to 0.08 ML, the heat of adsorption decreases linearly with coverage and is well described by the best-fit line $-\Delta H_{\text{ad}} = (200.-295 \theta)$ kJ/mol, where θ is the coverage in ML. At 0.08 ML, the negative slope abruptly increases in magnitude. From 0.08 to 0.115 ML, the heat of adsorption is well described by the linear best-fit line $-\Delta H_{\text{ad}} = (380-2466 \theta)$ kJ/mol. At 0.115 ML, the negative slope abruptly decreases in magnitude to near zero. Between 0.115 and ~ 0.28 ML, the heats of adsorption remain almost constant at approximately 85 kJ/mol. This indicates that there exists a transition layer between bulk multilayer phenol and the first chemisorbed layer. By 0.30 ML, we form multilayers of bulk phenol and the heat of adsorption becomes constant at 72.2 ± 1.0 kJ/mol, where the error bars are the run-to-run standard deviation on the mean of the average heat from 0.30 to 0.45 ML. This agrees well with the literature values for the heat of sublimation of phenol. Averaging the three literature values given by NIST gives a standard heat of sublimation of 69.0 kJ/mol at 298 K.^{19–21} Using the gas phase and solid phase heat capacities of phenol,

this average may be adjusted to the experiment temperature of 150 K, giving a standard enthalpy of sublimation of 71.2 kJ/mol. This value agrees within 1 kJ/mol of our measured value. These measurements indicate that the first layer of chemisorbed phenol is completed at 0.115 ML, which is within the error of the ideal coverage of 1/9 ML for a (3×3) structure. Thus, each phenol occupies approximately nine Ni atoms at saturation. To the best of our knowledge, there is no information as to whether phenol forms an ordered structure on the Ni(111) surface. The saturation coverage of benzene on Ni(111) is 0.13 ML (i.e., 7.7 Ni atoms per benzene) at 90 K.¹⁶ This larger area per phenol is not surprising, since it has the extra OH group.

Heat of Adsorption of Molecular Phenol on Pt(111) at 90 K. Figure 3 shows the heat of adsorption of phenol on the

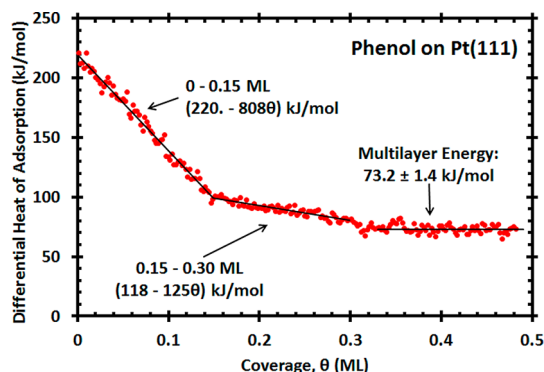


Figure 3. Differential heat of adsorption of molecularly adsorbing phenol on Pt(111) at 90 K as a function of adsorbed phenol coverage. Each data point represents a pulse of ~ 0.002 ML of phenol gas.

Pt(111) surface at 90 K. Here, phenol is expected to initially adsorb molecularly, parallel to the surface.^{7–9} Phenol adsorbs initially with a heat of adsorption of 220 kJ/mol. From 0–0.15 ML, the heat of adsorption decreases linearly with coverage and is well described by the best-fit line $-\Delta H_{\text{ad}} = (220 - 808\theta)$ kJ/mol. Our saturation coverage of the first layer is within error of that expected for a $(\sqrt{7} \times \sqrt{7})$ R19.1° structure, which corresponds to a coverage of 1/7 = 0.143 ML. Lu et al.⁸ adsorbed phenol from aqueous solutions onto a Pt(111) electrode at room temperature and observed a (3×3) structure at saturation using LEED and HREELS, which corresponds to 1/9 ML. Our coverage in UHV may be larger due to the absence of water solvent and the lower adsorption temperature used here.

From 0.15–0.30 ML, the heat of adsorption decreases much more slowly and is well described by the best-fit line $-\Delta H_{\text{ad}} = (118 - 125\theta)$ kJ/mol. The presence of this transition layer agrees well with previous TPD experiments, which found that the second phenol layer binds slightly more strongly, compared to bulk multilayer phenol, by evidence of a higher desorption peak at 225 K (compared to 195 K for the multilayer).⁹ By ~ 0.3 ML, bulk-like multilayers of phenol are formed and the heat of adsorption becomes constant at 73.2 ± 1.4 kJ/mol, where the error bars are the run-to-run standard deviation on the mean of the average heat from 0.30 to 0.48 ML. Adjusting the standard enthalpy of sublimation reported for bulk phenol (solid) at 298 K^{19–21} to 90 K using the gas phase and solid phase heat capacities of phenol results in a literature enthalpy of 71.9 kJ/mol. This value agrees within 1.3 kJ/mol with the heat of multilayer adsorption measured in this work.

DISCUSSION

Energetics of Adsorbed Phenol. The measured enthalpy of molecular adsorption at 150 K on Ni(111) (Figure 2) and at 90 K on Pt(111) (Figure 3) may be used to calculate the heats of formation of phenol on both surfaces. These heats for Ni(111) and Pt(111) are compared directly in Figure 4, and

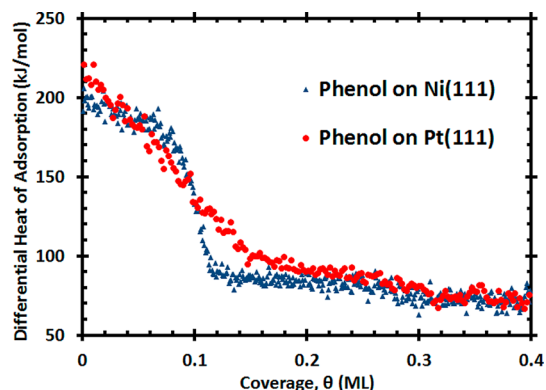


Figure 4. Comparison of the differential heat of adsorption of phenol on Ni(111) at 150 K and Pt(111) at 90 K as a function of adsorbed phenol coverage.

seen to be similar. We use the integral heat determined from the best fit lines for each adsorption curve up to a coverage of 1/9 ML. The thermodynamic cycles in Figure 5 show how to

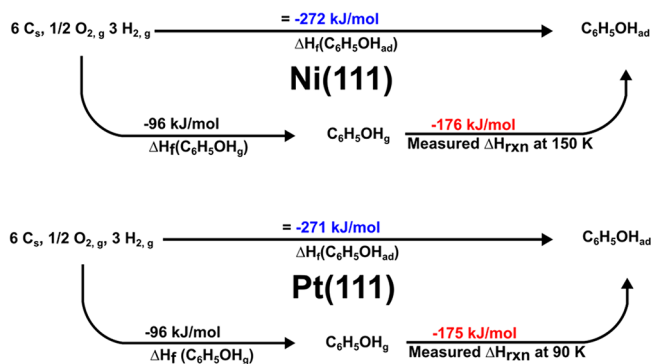


Figure 5. Reactions used to determine the heat of formation of molecularly adsorbed phenol on the Ni(111) and Pt(111) surfaces. The values in red correspond to the integral enthalpy of adsorption measured at 90 K for Ni(111) and 150 K for Pt(111) for the first 1/9 ML of coverage. The values in blue correspond to the resulting heats of formation of adsorbed phenol ($\text{C}_6\text{H}_5\text{OH}_{\text{ad}}$).

extract the heats of formation of adsorbed phenol on both Ni(111) and Pt(111). On the left-hand side of the figure, all elements are in their standard states and therefore possess a heat of formation of zero. The first step at the bottom is simply the enthalpy of formation of gaseous phenol, -96 kJ/mol.^{19–21} The second step at the bottom is our integral enthalpy of adsorption measured by SCAC from 0 to 1/9 ML of coverage (-176 kJ/mol for Ni(111) and -175 kJ/mol for Pt(111)). Adding these values together results in the enthalpy of formation of adsorbed phenol, i.e., the top pathway: -272 kJ/mol for Ni(111) and -271 kJ/mol for Pt(111).

Since there is no decomposition of phenol in these experiments, our measured integral heat of adsorption is equal to the total phenol–metal bond enthalpy. Therefore, at

Table 1. Comparison of Present Calorimetric Integral Bond Energies of Phenol to Ni(111) at 150 K and Pt(111) at 90 K with Calculated Values at 0 K Using DFT with Periodic Boundary Conditions

phenol on Ni(111)			bond energy (kJ/mol)		reference
coverage	DFT functional/method	DFT site	DFT	calorimetry	DFT
1/9 ML	PBE	bridge	88	175	25
1/16 ML	PBE-D3 (includes vdW)	HCP hollow	96	190	26
phenol on Pt(111)			bond energy (kJ/mol)		reference
coverage	DFT functional/method	DFT site	DFT	calorimetry	DFT
1/25 ML	PW91	bridge	215	203	27
1/16 ML	PBE	bridge	112	194	28
1/16 ML	PBE	bridge	126	194	29
1/16 ML	PBE-vdW	HCP hollow	176	194	29
1/16 ML	revPBE-vdW	HCP hollow	105	194	29
1/16 ML	PW86-vdW2	HCP hollow	100	194	29
1/16 ML	PBE-dDsC	bridge	208	194	30
1/16 ML	optB88-vdW	bridge	199	194	28
1/16 ML	PBE-D3 (includes vdW)	HCP hollow	172	194	26

1/9 ML coverage, the phenol–Ni(111) bond enthalpy is -176 kJ/mol and the phenol–Pt(111) bond enthalpy is -175 kJ/mol. These bond enthalpies may be converted into bond energies by changing sign and subtracting RT . This results in a phenol–Ni(111) bond energy of 175 kJ/mol and phenol–Pt(111) bond energy of 174 kJ/mol, both averaged up to $1/9$ ML.

Previous TPD work studying adsorbed phenol on Pt(111) shows a clearly resolved peak at 225 K, which corresponds to a second layer, above the 195 K peak for multilayer phenol.⁹ This second layer, with a slightly higher heat of adsorption than the multilayer, is also clearly observed in Figure 3. Averaging the data points in Figure 3 from 0.15 to 0.30 ML gives an average adsorption enthalpy of 89.5 kJ/mol for this second layer. Converting this value to an activation energy of desorption (E_{des}) by subtracting $1/2RT$ (as explained elsewhere²²) gives $E_{\text{des}} = 89.1$ kJ/mol. Using this E_{des} in the first-order Redhead equation²² together with its reported TPD peak temperature of 225 K gives a prefactor for desorption of this second layer of $2.5 \times 10^{20} \text{ s}^{-1}$.

Comparison of Phenol Adsorption on Ni(111) and Pt(111). A direct comparison of the heats of adsorption of phenol on Ni(111) at 150 K and Pt(111) at 90 K is shown in Figure 4. On the basis of the bond energies measured in this work, phenol binds with comparable bond strength to both surfaces. The 1 kJ/mol difference in the integral bond energy at $1/9$ ML is well within the error in our absolute calibration (up to 3%).¹¹ By “integral bond energy” here, we mean the average adsorption energy between zero coverage and the stated coverage, or $1/9$ ML here. However, this difference changes depending on the chosen coverage. Initially, phenol binds to Pt(111) more strongly than Ni(111), up to a coverage of ~ 0.04 ML. From ~ 0.04 to ~ 0.10 ML, the differential heat of adsorption of phenol on Ni(111) is stronger. The higher heat below 0.04 ML on Pt may be due to a larger fraction of step sites on Pt(111), the removal of which requires higher annealing temperatures than Ni(111). Step sites are known to bind aromatic molecules more strongly than terraces on Pt(111).²³ From ~ 0.10 ML up until the saturation of the second layer, phenol binds stronger to Pt(111) again.

The similarity in first-layer heats of phenol adsorption between Ni(111) and Pt(111) above was also seen for benzene.¹⁶ This was explained for benzene as being due to a

cancellation of two opposing effects: stronger intrinsic covalent bonding for Ni–C compared to Pt–C bonds but stronger van der Waals (vdW) attractions for Pt.¹⁶ The similarity for phenol is not surprising, since the nature of the bonding seems to be very similar to that of benzene, as indicated by the similar integral bond energies for benzene (166.9 kJ/mol at $1/9$ ML on Ni(111) and 160.7 kJ/mol at $1/9$ ML on Pt(111))¹⁶ compared to those above for phenol. There seems to be little contribution to the adsorption energy from oxygen-to-metal bonds, since O–Ni bonds should be >50 kJ/mol stronger than O–Pt bonds.²⁴

Comparison to DFT Calculations. The heats of molecular adsorption of phenol onto Ni(111) and Pt(111) measured in this work may be used as benchmarks for comparison to theoretical calculations. Table 1 gives several calculated bond energies from various DFT methods and the measured integral bond energy of adsorbed phenol at the same coverage. As reviewed in the Introduction, previous experimental measurements on both Ni(111) and Pt(111) had indicated that the phenol adsorbs molecularly (without bond breaking) with its aromatic ring lying parallel to the metal surface under the conditions of the present calorimetric measurements. The DFT results here are also for such a structure. They do not include zero-point energy corrections. The DFT results for each surface are divided into two sections, those that employ corrections for van der Waals (vdW) forces and those that do not.

The calculated DFT results for phenol adsorption on Ni(111) underestimate the adsorption energy strength by 87 – 94 kJ/mol, regardless of the inclusion of vdW corrections, which was done with only one functional, PBE-D3. The calculated DFT results for phenol adsorption on Pt(111) range from underestimating the energy by 94 kJ/mol to overestimating the energy by 12 kJ/mol. Results that include vdW corrections were less likely to underestimate the energy. However, in some cases, vdW-corrected functionals also underestimated the adsorption energy to Pt(111) by ~ 100 kJ/mol. For the closely related system of benzene on Ni(111), optB86b-vdW and optB88-vdW gave adsorption energies of 211 and 173 kJ/mol, respectively, both close to our SCAC value of 188 kJ/mol.¹⁶ Therefore, we believe that the very low value for the DFT energy on Ni(111) for the one study that included vdW corrections in Table 1 is probably due to a problem with that particular method (PBE-D3) for Ni(111),

rather than due to a general problem with vdW corrections in DFT for Ni(111). As seen in Table 1, this same method only underestimates the adsorption energy for Pt(111) by 22 kJ/mol.

The experiments in Table 1 are at 150 and 90 K, whereas the DFT values are for 0 K. The heat capacity difference between solid phenol and gaseous phenol is only 14 J/(mol K) at 150 K and drops to ~ 10 J/(mol K) at 90 K,³¹ and this difference must approach zero at 0 K. Thus, we expect the average heat capacity difference between adsorbed phenol and gaseous phenol to be < 30 J/(mol K) in the range from 0 K to the measurement temperature of 90 or 150 K. Thus, the temperature difference between the experiments and the DFT results in Table 1 should contribute less than 5 kJ/mol to the energy differences seen there.

To the best of our knowledge, there is no experimental knowledge of the preferred adsorption site of phenol on either surface. Theoretical studies that do not include vdW corrections systematically calculate the strongest adsorption to be at bridge sites. Studies that use vdW corrected functionals vary in their adsorption site, preferring either bridge or HCP hollow sites. For phenol, the adsorption site is defined as the site over which the aromatic ring is centered.

CONCLUSIONS

On Ni(111), phenol adsorbs molecularly at 150 K with a decreasing heat of adsorption in the first 0.08 ML well fit by $-\Delta H_{\text{ad}} = (200 - 295 \theta)$ kJ/mol. From 0.08 to 0.115 ML, the heat of adsorption drops more rapidly and is well fit by $-\Delta H_{\text{ad}} = (386 - 2529 \theta)$ kJ/mol. On Pt(111), phenol adsorbs molecularly at 90 K with a decreasing heat of adsorption in the first 0.15 ML well fit by $-\Delta H_{\text{ad}} = (220 - 808 \theta)$ kJ/mol. On both Ni(111) and Pt(111), phenol adsorbs with a nearly constant heat of adsorption above 0.3 ML of 72–74 kJ/mol, which is the value for multilayer solid phenol. Using the known enthalpies of the gas-phase phenol, we find a standard enthalpy of formation of adsorbed phenol (ΔH_f^0) of -272 kJ/mol on Ni(111) and -271 kJ/mol on Pt(111).

These measured energies were compared to DFT from many different studies. We found that DFT calculations that neglect van der Waals corrections are more likely to underestimate this adsorption energy, while many DFT functionals that include van der Waals corrections are more accurate. However, some calculations on both surfaces, even those with vdW corrections, still grossly underestimated the adsorption energy of phenol.

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Notes

The authors declare no competing financial interest.

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