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Methanol Decomposition on Ni(111) and O/Ni(111)

Henrik Öström
Stockholm University

Bingjie Zhang
Chapman University, binzhang@chapman.edu

Tiffany Vallejo
Chapman University

Bryn Merrill
Chapman University, merri152@mail.chapman.edu

Jeremy Huang
University of California - Berkeley

See next page for additional authors

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Authors

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Henrik Öström,[1] Bingjie Zhang,[2] Tiffany Vallejo,[2] Bryn Merrill,[2] Jeremy Huang,[3] and Jerry LaRue[2,a)]

AFFILIATIONS

[1] Department of Physics, AlbaNova University Center, Stockholm University, SE-10691 Stockholm, Sweden
[2] Schmid College of Science and Technology, Chapman University, Orange, California 92866, USA
[3] University of California at Berkeley, Berkeley, California 94720, USA

[a)] Author to whom correspondence should be addressed: larue@chapman.edu

ABSTRACT

Methanol decomposition on Ni(111) surfaces has been studied in the presence and absence of oxygen using temperature-programmed desorption and temperature-dependent sum frequency generation spectroscopy. Under both conditions the C–H and O–H bonds break, forming carbon monoxide and atomic hydrogen on the surface. No C–O bond scission was observed, limiting the number of reaction pathways. The O–H bonds break first (>150 K), forming surface methoxy, followed by C–H bond breakage (>250 K). All atomic hydrogen desorbs from the surface as H_2 through H+H recombinative desorption. H_2 desorbs at a higher temperature in the presence of oxygen (>300 K) than the absence of oxygen (>250 K) as the oxygen on the surface stabilizes the H atoms, forming surface hydroxide (OH). The surface oxygen also appears to stabilize the O–H and C–H bonds, leading to slightly higher dissociation temperatures. The CO molecules occupy both the bridge sites and the top sites of the Ni atoms as surface H appears to force the CO molecules to the top sites. There is a slight blueshift in the C–O bond vibration for both the O covered and O free surfaces due to CO being more mobile. On the O free surface, the C–O peak width broadens as low-frequency modes are activated. Finally, CO desorbs between 350 and 400 K.

INTRODUCTION

Catalysts are used to reduce energy consumption, minimize pollution, enable the synthesis of high-value molecules, and increase food production. They accomplish these outcomes by lowering the activation energy barriers for desired reaction pathways, resulting in more efficient and selective chemical reactions. Despite these successes, there is a need for better catalysts to combat global challenges, such as climate change and pollution. Methanol (CH_3OH) is an important chemical intermediate. This process is critical for a green economy as syngas is available from renewable sources, such as biomass.

Ni is an active methanation catalyst, converting CO and H_2 into methane.[1–4] The step sites on the Ni surface are more active in breaking the C–O bond than the terrace sites, with the step sites having a 1 eV lower energy barrier for CO dissociation.[5] Terraced Ni surfaces have the potential to open up additional reaction pathways where the C–O bond remains intact, creating products such as methanol. Much work has previously been done on methanol, methoxy, and their decompositions on Ni(111).[6–19] Density-functional-theory work of formaldehyde and methanol synthesis from CO and H_2 on a terraced Ni(111) surface have showed that hydrogenation of CO is favored over desorption or dissociation of CO, forming the formyl radical (HCO) or its isomer, COH.[1] Subsequent hydrogenation leads to formaldehyde (CH_2O), methoxy (CH_3O), and methanol (CH_3OH). These reactions require high pressures. Under ultrahigh vacuum conditions, CO and H desorb from the clean Ni(111) surface prior to reacting.[20,21] The reverse of methanol formation (i.e., its dissociation) has been extensively studied on Ni(111) under ultrahigh vacuum (UHV) conditions.[6–12,19] Less is known about how oxygen affects the methanol decomposition pathway on Ni(111).

Here, we compare the decomposition pathways of methanol on the terraced Ni(111) surface with the oxygen-covered Ni(111) surface using a temperature programmed desorption (TPD) and temperature dependent sum-frequency generation (TD-SFG) spectroscopy. We show that the presence of O slightly alters the dissociation pathway, with the biggest difference being the stabilization of surface H through the formation of OH.

EXPERIMENTAL

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure below 1×10^{-10} Torr, in combination with a high-power femtosecond Ti:sapphire laser system. The Ni(111) crystal was cleaned *in situ* by cycles of Ar ion sputtering at 1 kV, followed by resistive annealing to 1100 K until low energy electron diffraction (LEED) showed a sharp 1×1 pattern. In order to obtain controlled dosing with minimal gas load and wall reactions, methanol and oxygen were dosed via a collimated channel plate doser at a sample temperature of 105 K. Both methanol and oxygen exposures were ~1 L. For oxygen, we expected this exposure to give the (2×2)O/Ni(111) surface, which was confirmed using LEED.[22]

TPD traces were recorded using a Hiden mass spectrometer while heating the sample from 105 to 600 K at a constant rate of ~45 K/min. The Ni(111) crystal is shielded from the mass spectrometer filament by a metal plate, minimizing any potential electron-induced chemistry during TPD. TD-SFG spectroscopy was recorded separately from TPD using a heating rate of ~3 K/min. For SFG, a femtosecond laser amplifier system provided 800 nm with a pulse energy of up to 3.7 mJ per pulse and a pulse length of 50 fs at a repetition rate of 1 kHz. The laser was combined with an optical parametric amplifier with a noncollinear difference frequency generation (nDFG) stage. For the present experiment, the nDFG was set to 2000 or 3000 cm^{-1}, which yielded an IR spectrum of width ~300 cm^{-1}, to overlap with the C–O or C–H stretching vibrational range, respectively. Together with spectrally narrowed 800 nm pulses, these pulses were used to perform broadband vibrational SFG spectroscopy. Sum-frequency generation is a second-order nonlinear optical process where two incident light waves are combined to yield a wave with the sum-frequency of the incoming waves, conserving both energy and momentum, which gives rise to surface sensitivity since, within the dipole approximation, the sum-frequency signal is only generated when inversion symmetry is broken. If one of the incoming waves is spectrally overlapped with adsorbate vibrations, a resonant enhancement can occur, and vibrational spectroscopy can be performed. The SFG signal was spectrally resolved and recorded using an optical spectrograph equipped with an intensified CCD camera. The experimental frequency resolution was typically set to ~8 cm^{-1} and was limited by the spectrometer resolution and spectral width of the 800 nm up-conversion pulses. For the temperature dependent data, the intensity of the up-conversion light was increased by reducing the spectral resolution to 12 cm^{-1}. The up-conversion frequency was subtracted from the observed frequency, and the spectra are presented on the vibrational energy scale. The spectra were frequency calibrated in the infrared using the known vibrational frequency of adsorbed CO. Typical pulse energies were around 5 μJ each for the infrared and up-conversion pulses. The beam diameter of the up-conversion pulse at the sample was around 500 μm, while the mid-infrared pulse was slightly larger.

The SFG spectral intensity can typically be well described by the square of the sum of a non-resonant susceptibility, $\chi_{NR}^{(2)}$, and the vibrational resonant susceptibilities, $\chi_{R}^{(2)}$.[23] The spectra were fitted using this model, and the non-resonant background, as measured on the clean sample, was taken as a spectral profile of the infrared pulses. The phase shift between resonant and non-resonant contributions typically leads to an asymmetric line shape and can give rise to a small shift between the resonance position and the peak maximum.

RESULTS AND DISCUSSION

Figure 1 shows TD-SFG spectra for methanol dissociation on Ni(111) and O/Ni(111) at the C–O vibrational resonance and the C–H vibrational resonances. These data are accompanied by TPD traces of the desorbing products. Due to the higher heating rates used in TPD, similar features will be shifted to slightly higher temperatures in the TPD traces than the SFG spectra. In our estimate, the shift will be between 20 and 25 K, though it is dependent on the kinetic prefactor of the desorbing species. The intensities of the SFG fits are shown in Fig. 2 for methanol decomposition on Ni(111) and Fig. 3 for methanol decomposition on O/Ni(111). For both sets of data, the TPD data are shown below the SFG intensities for comparison.

For vibrational frequency assignments, we compared our data to previously reported methanol, methoxy, and CO vibrational assignments for gas phase and adsorbed species on Ni(111).[18,24–29] In the C–H vibrational frequency region, methanol has one CH_3 symmetric stretch ($\omega_{\mathrm{CH_3}}^{s(a')}$) and two CH_3 asymmetric stretches ($\omega_{\mathrm{CH_3}}^{d(a)}$ and $\omega_{\mathrm{CH_3}}^{d(a')}$). Due to an increase in symmetry, methoxy has one CH_3 symmetric stretch ($\omega_{\mathrm{CH_3}}^{s(a_1)}$) and one CH_3 asymmetric stretch ($\omega_{\mathrm{CH_3}}^{d(E)}$) in this region, as well as an additional overtone band of the CH_3 symmetric bend ($\omega_{\mathrm{CH_3}}^{OT}$). In the C–O vibrational frequency region, we observe the C–O stretch frequency for CO, which depends on the adsorption site ($\omega_{\mathrm{CO}}^{top}$ for top-site CO and $\omega_{\mathrm{CO}}^{b/h}$ for bridge- or hollow-site CO).

Figure 4 shows temperature slices of the SFG spectra between 110 and 200 K. At low temperatures (~110 K), methanol adsorbs molecularly on the Ni(111) surface. Previous studies show that methanol sits on the top site on the Ni(111) surface and is stabilized on transition metal surfaces by means of dipole-induced dipole interactions.[1] The oxygen atom forms a bond with the Ni atom, while the remainder of the molecule sticks up at an angle from the surface. After the first layer is saturated, methanol continues to adsorb, forming methanol overlayers (methanol ice). TPD traces show molecular methanol desorbing at 150 K, and at this temperature, there is a decrease in intensity from methanol in the SFG spectra as the methanol overlayers desorb, leaving a single methanol layer on the Ni(111) surface.

On the Ni(111) surface, the methanol multilayer desorbs around the same temperature that the methanol O–H bond is broken, giving rise to surface H ($\mathrm{H_{O\text{–}H}}$). In the presence of O, methanol O–H bond breakage occurs at a slightly elevated temperature of ~20 K higher, suggesting that the surface O slightly stabilizes molecular methanol. After O–H bond scission, the $\mathrm{H_{O\text{–}H}}$ atoms remain on the surface, and in the absence of O, they sit in the fcc hollow sites.[11] In the presence of O, they form OH with the surface

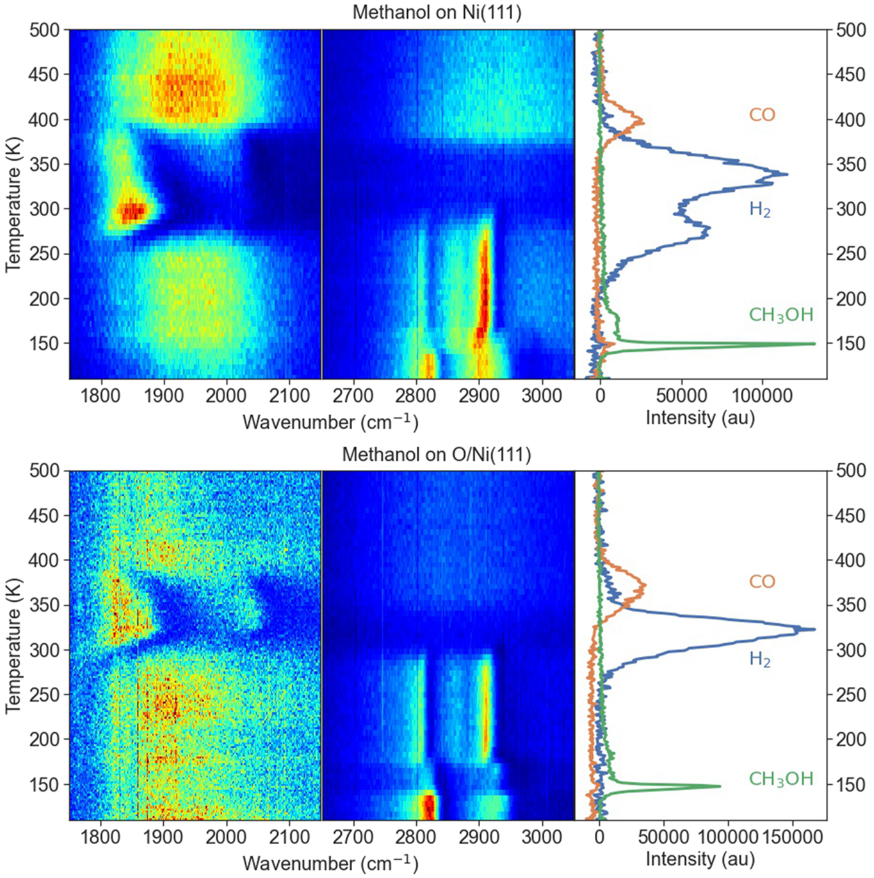

FIG. 1. False color plot of TD-SFG spectra of the (left) C–O vibrational frequency region, (center) C–H vibrational frequency region, and (right) TPD traces for methanol decomposition on Ni(111) (top) and O/Ni(111) (bottom).

O.[19] These results are consistent with most of the prior studies on methanol dissociation on Ni(111),[6–10,13,14,18] with the primary exception being the findings by Carey *et al.*[19] They found that methanol does not dissociate into methoxy on the clean Ni(111) surface and that dissociation of methanol to methoxy in the presence of O occurs already at 100 K.[19] The authors conducted their experiments at constant temperatures. At 155 K, they reported that methanol adsorbs in its molecular form, while at 180 K and above, methanol only transiently adsorbs before desorbing, leading to a maximum coverage of ≤0.04 ML. It may be that on a clean Ni(111) surface, a high coverage of methanol is a prerequisite for methoxy formation. Other studies have reported methanol dissociation on

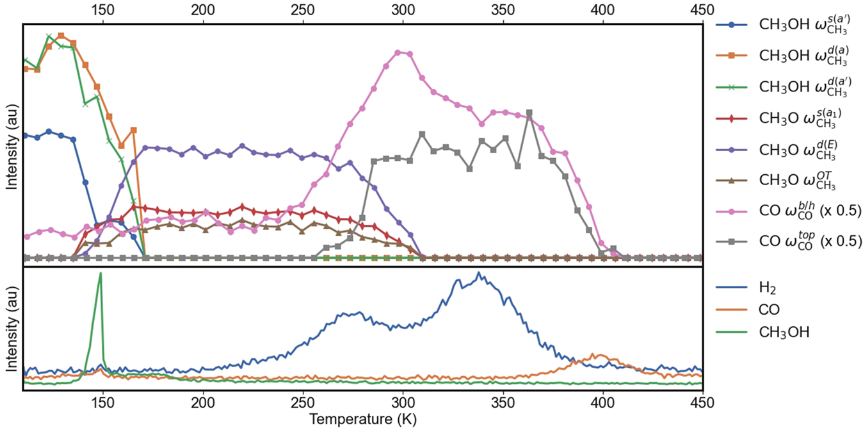

FIG. 2. Methanol decomposition on Ni(111). (Top) Peak intensities from fits for the TD-SFG vibrational resonances of methanol, methoxy, and CO as a function of temperature. (Bottom) TPD traces of the desorbing products as a function of temperature.

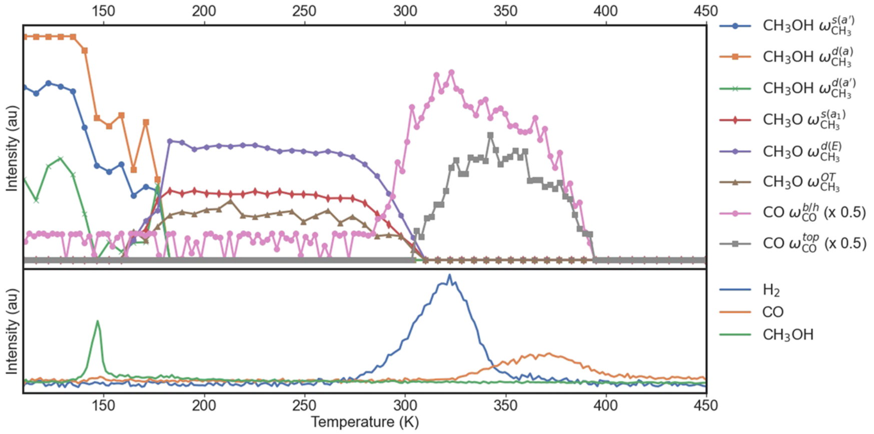

FIG. 3. Methanol decomposition on O/Ni(111). (Top) Peak intensities from fits for the TD-SFG vibrational resonances of methanol, methoxy, and CO as a function of temperature. (Bottom) TPD traces of the desorbing products as a function of temperature.

Ni(111) using a collimated beam of methanol at elevated temperatures (200–500 K),[6,8] though these studies appear to use a higher flux of methanol and may achieve a higher surface coverage. More studies are needed to fully explain these discrepancies.

The structure of methoxy on Ni(111) surfaces has been previously investigated.[13–18] From these studies, it was determined that methoxy sits vertically on the fcc hollow sites of the Ni surface, with the O down. There is not a large change in the CH_3 vibrational resonant frequencies between the presence and absence of O. Based on these similarities between spectral signatures of methoxy on the Ni(111) and O/Ni(111) surfaces, we propose that the vertical structure is preserved in the presence of surface O. Since the O atoms also occupy the hollow sites, it is not clear if the methoxy remains in the hollow sites or shifts to bridge or top sites. We predict, that due to charge repulsion with the O atoms and the similar CH_3 vibrational resonant frequencies, that the methoxy shifts to bridge sites. If methoxy were to move to the top sites, we would expect a larger shift toward gas phase values.

In the presence and absence of surface O, all the C–H bonds break between 250 and 300 K, leading to more surface H (H_{C-H}). At 300 K, the C–H resonance signals disappear, and the non-resonant background is suppressed in the C–H region as the methoxy decomposes to CO and H. This is confirmed in the C–O vibrational resonance region, where the CO vibrational resonance appears. The initial methoxy C–H bond breakage is followed by a rapid dissociation of the remaining two C–H bonds as we do not detect any CH_2O or CHO on the surface. This is likely because the first C–H bond breakage has the highest energy barrier. CH_2O would be particularly observable as, unlike the other intermediate species, it sits horizontal on the surface, with both the C and O forming surface bonds.[11]

The resulting CO molecules occupy the top sites and the bridge sites on both surfaces. CO on Ni(100) adsorbs only on the top sites; however, CO can be forced to the bridge and hollow sites through the co-adsorption of H.[30,31] On Ni(111), CO has been observed to occupy top, bridge, and hollow sites, depending on coverage, and these adsorption sites can be determined from the internal C–O stretch frequency, as the higher coordinated CO is with the surface, the lower its internal stretch frequency.[28,32] CO mainly occupying top sites at high coverages of $\theta > 0.50$ monolayers (ML), where ML is defined as the ratio of adsorbate molecules to Ni(111) surface atoms.[32] From this, we would expect little to no top-site CO as previous studies have shown that CO coverage from methanol dissociation saturates at a low coverage of 0.3 ML on Ni(111).[8] Our results, however, show strong top-site CO SFG signals. The surface

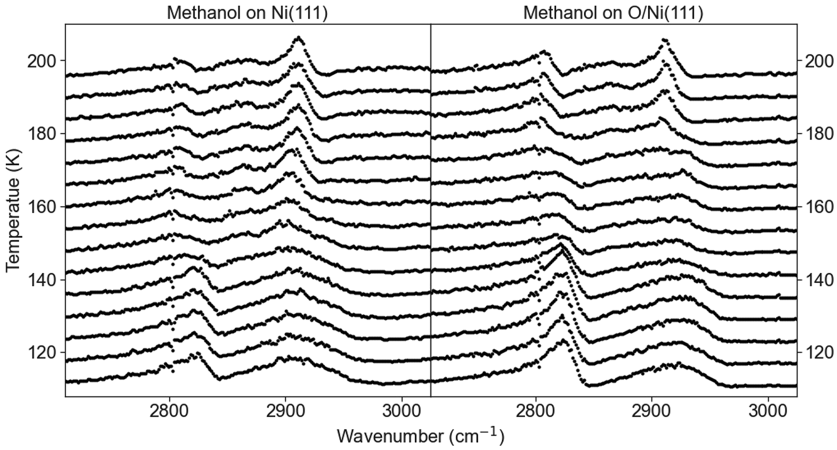

FIG. 4. Temperature slices of the SFG spectra showing the desorption of the methanol multilayer and the methanol to methoxy transition on (left) Ni(111) and (right) O/Ni(111). Around 150 K, the intensity of the methanol peak decreases, marking the desorption of the methanol overlayer. On the Ni(111) surface, the methanol starts to dissociate around the same temperature, giving rise to the methoxy peaks. On the O/Ni(111) surface, the methanol to methoxy transition occurs around 20 K higher in temperature.

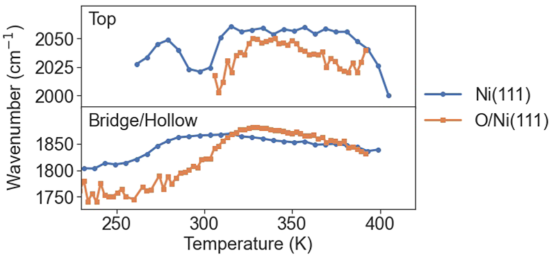

FIG. 5. The internal C–O stretch frequency as a function of temperature for (top) top-site CO and (bottom) bridge-site or hollow-site CO on Ni(111) and O/Ni(111). The CO signal below ∼250 K on the Ni(111) surface and below ∼270 K on the O/Ni(111) surface arises from low levels of CO already present on the surface, with CO occupying hollow sites. As methoxy decomposition occurs, these CO molecules move to the bridge sites. The blueshift of bridge-site CO, including those resulting from methoxy decomposition, can be attributed to the activation of low-frequency vibrational modes, leading to larger adsorbate motion on the surface. After 300 K, H_2 and CO desorb from the surface, reducing CO intermolecular repulsions for all CO species and lowering the CO-surface adsorption energy. This results in a reduction of the C–O bond strength, leading to a redshift in the C–O stretch frequency.

H that results from methanol decomposition may force some CO molecules to occupy the top sites, leading to a higher concentration of top-site CO. Due to the nonlinear intensity in the SFG spectra, we cannot make quantitative statements about the relative amount of top-site CO vs bridge-site CO.

Molecular hydrogen desorbs through H+H recombinative desorption.[33,34] This process occurs on the Ni(111) at 250 K and is shifted up to 300 K in the presence of O due to the formation of surface OH. For Ni(111), the desorption of H_2 occurs at a lower temperature than the C–H bond breakage, creating two distinct H_2 peaks in the TPD traces. The first peak has an area 1/3 of the second peak as it arises from the H_{O-H} atoms prior to C–H bond cleavage. Once the C–H bonds start to break around 300 K, the H_{C-H} atoms associatively desorb as H_2 in the second peak. For O/Ni(111), the H_2 desorption temperatures for H_{O-H} and H_{C-H} overlap, giving rise to a single H_2 desorption peak. As SFG is blind to surface H, these processes were observed from the transition from methoxy to CO in the SFG spectra and the H_2 desorption peaks in TPD.

As CO is formed from methoxy dissociation, the internal stretch frequencies for the bridge-site CO blueshift to higher energies (see Fig. 5). Such a blueshift has been observed previously for c(4 × 2) CO/Ni(111) and was attributed to coupling to low-frequency vibrational modes that are increasingly activated,[28] which leads to larger adsorbate motion on the surface. In the present case, the blueshift occurs with decreasing methoxy on the surface and while the H atoms originally associated with the O–H bond are desorbing from the Ni surface. The combination of these allows for more freedom of motion among the adsorbed CO molecules. Above 300 K, the internal C–O stretch frequency starts to slowly redshift back. We propose that this is due to less intermolecular repulsions from surface H and other surface CO molecules. Around 300 K, the H_{C-H} atoms start to desorb, reducing H–CO repulsions, and at around ∼50 K higher temperatures, CO starts to desorb, reducing CO–CO repulsions. The top-site CO on both surfaces shares these

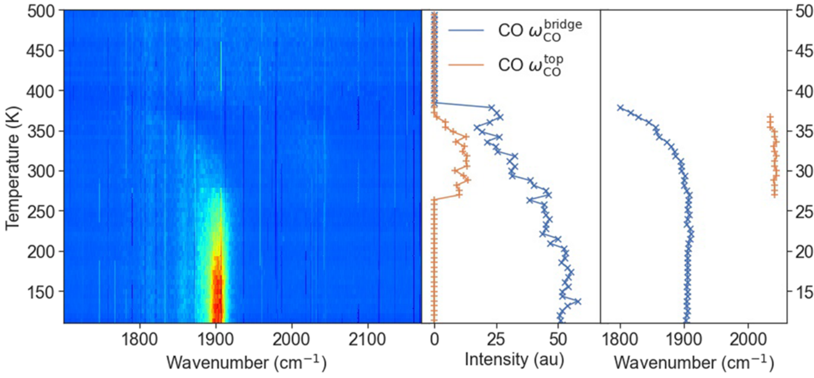

FIG. 6. CO on Ni(111). (Left) False color plot of TD-SFG spectra. The amplitudes (middle) and frequencies (right) of the TD-SFG fits for the internal C–O stretch for CO ω_{bridge} (×) and CO ω_{top} (+). As the bridge-site peak shifts to lower frequency toward 1800 cm^{-1}, it approaches the limit of detection, increasing the uncertainty in the intensity of the peak.

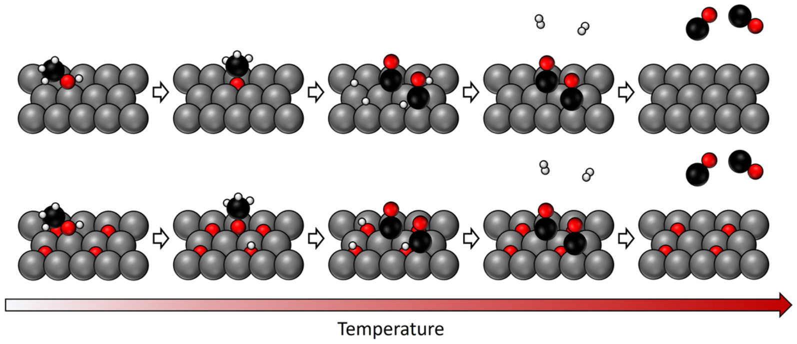

FIG. 7. Schematic of methanol decomposition as a function of temperature on Ni(111) (top) and oxygen-covered Ni(111) (bottom). The O–H bond is the first to break, forming methoxy. The H remains on the surface and, in the case of O/Ni(111), forms OH. As the temperature increases, the C–H bonds break in rapid succession. The resulting CO sits on top and bridge sites. The H atoms desorb through associative desorption. Finally, the CO molecules desorb, leaving a clean surface. No C–O bond scission was observed.

general trends. It is interesting to note around 300 K, the top-site CO frequency temporarily and rapidly redshifts on Ni(111). This occurs as the methoxy signal disappears and the surface $H_{C\text{–}H}$ start to desorb. At 400 and 375 K, CO desorption peaks from the Ni(111) and O/Ni(111) surfaces, respectively, in the TPD traces, with all CO desorbed when the surface is further heated by 25 K. The CO vibrational resonances disappear in the TD-SFG spectra near the maximum CO TPD desorption temperatures as the TD-SFG features are shifted 20–25 K lower in temperature due to the slower heating rates. Following the disappearance of the CO vibrational resonance, the non-resonant background re-emerges in the C–H resonance region.

In both the Ni(111) and O/Ni(111) surfaces, we see evidence of low levels of CO contamination prior to methanol and methoxy decomposition. The C–O bond frequency from the contaminated CO is downshifted from typical bridge sites, suggesting that the presence of methanol and methoxy may force the CO molecules down to the hollow sites.

We recorded TD-SFG of CO on Ni(111) for comparison (see Fig. 6). The results are generally consistent with temperature dependent infrared absorption spectroscopy reported by Persson and Ryberg.[28] From 110 to 270 K, the bridge-site CO slight blueshifts from 1903 to 1908 cm^{-1} and the peak width broadens from 10 to 17 cm^{-1}. The blueshift is due to CO being more mobile on the surface, as low-frequency modes are activated. The broadening is related to the temperature-dependent vibrational phase relaxation through coupling to the frustrated rotation (ω_{rot}).[27,28] We observe a similar broadening in the CO signal from methanol on Ni(111), but not on the O covered Ni(111) surface. It appears that surface O may disrupt vibrational phase relaxation through the frustrated rotation. At 270 K on the CO/Ni(111) surface, we observed a drastic redshift in the bridge-site CO, along with a decrease in the intensity of the SFG signal. This redshift corresponds to the rise of top-site CO at 2041 cm^{-1}, which are not observed at lower temperatures. Top-site and bridge-site CO remain present until the CO signal disappears around 380 K. TPD traces of CO on Ni(111) show CO desorbing from the surface between ~350 and ~450 K. Unlike Persson and Ryberg, we did not observe a blueshift in the top-site CO, though this may be due to the low signal-to-noise ratio of this feature.

CONCLUSION

We have studied methanol decomposition on the Ni(111) and O/Ni(111) surfaces using TPD and TD-SFG. The combination of these techniques provides a rich picture of the temperature dependent chemistry that occurs on the Ni surface, as shown in Fig. 7. The presence of O on the surface only slightly alters the reaction pathway. Methanol decomposes on the Ni(111) surface with the breaking of the O–H bond, followed by the breaking of the C–H bonds, both in the presence and absence of O. The H remains on the surface prior to desorption. For the oxygenated surface, the H is stabilized by the presence of O, forming OH and increasing the desorption temperature. The O covered surface preserves the vertical structure of methoxy with the O end toward the surface. After methoxy dissociation, the CO molecules adsorb at both bridge and top sites. As the temperature continues to increase, prior to desorption, the CO internal stretch blueshifts to higher energies, consistent with mobile CO on the surface. After CO desorbs, all reactants have left the Ni surface. We observed no evidence of C–O bond breakage. These results will help to better understand how co-adsorbates affect the evolution of chemical reactions on catalytic surfaces, with the goal of creating more efficient and selective catalysts.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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