

Adsorption and Reaction of Formic Acid on a (2 × 2) NiO(111)/Ni(111) Surface. 3. IRAS Studies on the Characterization of Reaction Sites Using CO and the Behavior of Surface Hydroxyl Species

Taketoshi Matsumoto, Athula Bandara, Jun Kubota, Chiaki Hirose, and Kazunari Domen*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Received: November 25, 1997; In Final Form: February 11, 1998

The decomposition of formic acid on (2 × 2) NiO(111)/Ni(111) was studied by infrared reflection absorption spectroscopy (IRAS). Formic acid molecules adsorbed dissociatively on the surface to form formate which decomposed to H₂, CO₂, H₂O, and CO at 340–415 and 520 K. The vacant sites after the decomposition of formate were probed by the adsorption of CO at 100 K. On clean NiO(111) at 100 K, IRAS peaks of two types of adsorbed CO were observed at 2146 and 2079 cm⁻¹, which were assigned to the CO on fully-oxidized Ni cation sites and less-oxidized Ni cation sites, respectively. The CO peaks were not observed on the formate precovered surface. The IRAS peak of adsorbed CO at 100 K on the fully-oxidized Ni cation sites appeared when the surface was heated to decompose formate around 340–415 K. After decomposition at 520 K, the intensities of both peaks of CO were recovered to the initial intensities. It was thus concluded that the sites of decompositions at 340–415 and 520 K are the fully-oxidized Ni cation sites and less-oxidized Ni cation sites, respectively. The behavior of hydroxyl species produced by dissociative adsorption of formic acid was next investigated using deuterated formic acid (DCOOD). The hydroxyl species (–OD) formed by the dissociative adsorption of formic acid (DCOOD) was observed at 2536 cm⁻¹ below 343 K, while the isolated OD groups appeared at 2713 cm⁻¹ and around 500 K. The mechanism of decomposition of formate at each temperature is discussed.

Introduction

Considerable attention has been paid to the study about adsorptions and reactions of molecules on single-crystal oxide surfaces to understand the catalytic properties of oxides. The study of oxide surfaces lags behind that of metal and semiconductor surfaces since electron spectroscopies and infrared reflection absorption spectroscopy (IRAS) have been difficult to apply on such surfaces, especially in early times, because of the low electron conductivity and high transparency.¹ A recently developed technique to prepare epitaxially grown films of oxides on metal substrates enables us to apply these spectroscopies, and there has been a large interest in these surfaces in the past several years.^{2–13}

NiO single-crystal films on substrates of single-crystal metals are typical examples of epitaxial films applied to the study of adsorptions of molecules by several methods.^{4,5,7–13} The NiO(111) surface is known to be more active for chemical reactions than NiO(100) because Ni cations at the surface are at a lower coordination number.⁸ NiO(111) is reconstructed to the (2 × 2) structure terminated by oxygen atoms in a vacuum; thus trigonal pyramids of the microfacets are disposed in order.^{5,9}

A significant intermediate in the water–gas shift, methanol synthesis, and selective oxidation reactions has been considered to be the carboxylate species on the surface. One of the simplest way to produce carboxylate is dissociative adsorption of carboxyl acid on the surface as reported on TiO₂(100),¹⁴ NiO(100),⁴ NiO(111),^{7,8} MgO(100),¹⁵ ZnO(0001),¹⁶ and ZrO₂(100).¹⁷ Our group has investigated the adsorption and decomposition of formic acid on NiO(111) prepared by oxidation of Ni(111) under vacuum and steady-state conditions.^{10,11} It was found

that formic acid adsorbs on NiO(111) to form formate, even at 163 K, which decomposes to desorb as H₂, CO₂, H₂O, and CO at 340–415 and 520 K in a vacuum. Formates were found to be in tilted bidentate configuration in a vacuum and in both bidentate and monodentate configurations under a flow of formic acid. Formic acid on a thick layer of NiO(111) prepared on a Mo(110) substrate was reported to decompose at 555 K by Xu and Goodman.^{7,8} The question is why the formate decomposes at two different temperatures, 340–415 and 520 K, on our surface. Further examination of the behavior of formate and that of the hydroxyl species, which may play an important role in the decomposition of formate, is required.

In this work, we investigated the characteristics of the reaction sites for decomposition of formic acid on NiO(111) using CO molecules as a probe. The behavior of hydroxyl species during the decomposition of formic acid was also examined by using deuterated formic acid.

Experimental Section

The experiments were carried out in an ultrahigh vacuum chamber evacuated to 10⁻⁸ Pa, as described in detail in the previous papers.¹¹ The clean Ni(111) surface was prepared by Ar ion bombardment and annealing at 1023 K and characterized by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The NiO film was grown on the clean Ni substrate by the cycles of exposure to oxygen gas at 1000 langmuirs (1 langmuir = 10⁻⁶ Torr s, 1 Torr = 133 Pa) and 570 K and annealing at 650 K. The thickness of the NiO film was estimated to be 5–10 monolayers from the AES peak intensities. The hexagonal LEED pattern which indicates (2 ×

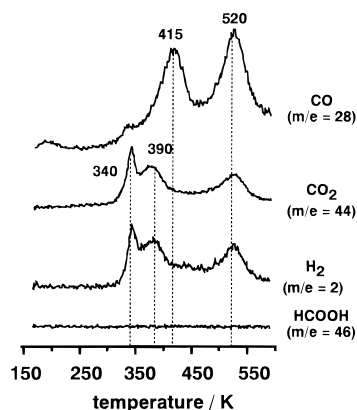


Figure 1. TPD spectra of the HCOOH-dosed NiO(111) surface. The surface was exposed to 10 langmuirs of HCOOH at 163 K.

2) NiO(111) was observed on the NiO film. It should be noted that the amount of oxygen on NiO(111) estimated by AES did not change after several repetitions of thermal desorption of formic acid or CO.

IRA spectra were acquired using a JEOL JIR-100 Fourier transform infrared spectrometer (FTIR) with an InSb/MCT composite detector. The resolution of the spectra was 4 cm^{-1} , and the spectra were averaged over 512 scans.

The commercially purchased gases were purified by passing them through a cold trap or by vacuum distillation before use. The amounts of exposure are derived from the apparent pressures displayed by an ionization gauge without any correction and calibration.

Results and Discussion

Characterization of Reaction Sites Using CO. Temperature-programmed desorption (TPD) spectra of formic acid on NiO(111) at 10 langmuirs are shown in Figure 1. The desorption of H_2 , CO_2 , and CO were observed as products of decomposition. The desorption of H_2O , which is the decomposition partner of CO, was not observed because of a high background signal. H_2 and CO_2 as the products of dehydrogenative decomposition desorbed in two temperature regions, 340–390 and 520 K. The presence of two regions indicates that there are two kinds of sites or two kinds of decomposition mechanisms. CO desorbed at 415 and 520 K. These desorptions can be classified into two groups which are observed around 340–415 and 520 K. Xu and Goodman reported that the decomposition temperature of formic acid on a thick layer of NiO(111) is around 555 K, where they used NiO(111) prepared on a Mo(110) substrate by evaporation of Ni in an oxygen environment.^{7,8} The desorption at 520 K in the present study may correspond to that at 555 K in their study. The aim of this study is to consider the reason formic acid is decomposed at two temperature regions.

CO molecule is often used to probe the adsorption sites as the vibrational frequency reflects the state of adsorption sites such as electronegativity. The IRA spectra of adsorbed CO on NiO(111) at 100 K and various exposures are shown in Figure 2. Two peaks were observed at 2146 and 2079 cm^{-1} . It is known that the high- and low-frequency peaks are corresponding to the adsorbed CO on the fully- and less-oxidized Ni cation sites (denoted as HF and LF sites), respectively.¹⁸ We consider that the HF sites are located at the (2×2) NiO(111) terrace since the frequency is close to that on other typical oxides.¹⁹ The frequency of the band for the CO on the LF sites is close to that of Ni metal surfaces, and the sites are regarded as defect

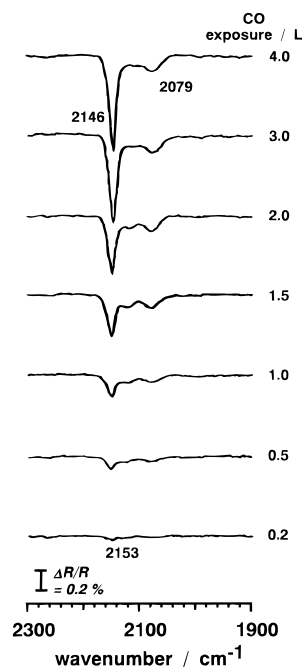


Figure 2. IRA spectra of CO adsorbed on the NiO(111) surface at 100 K with various exposures.

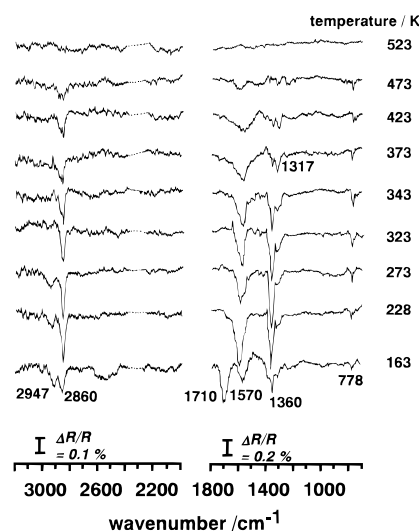


Figure 3. Temperature-dependent IRA spectra of formate adsorbed on NiO(111). The surface was first exposed to HCOOH (10 langmuirs) at 163 K and then heated to the stated temperatures.

sites such as oxygen vacancies, steps, or boundaries of crystal domains. The CO desorbed at 125 K, and no CO_2 was produced during thermal desorption, indicating that CO adsorbs only weakly without any reaction on NiO(111).

The temperature dependencies of the IRA spectra of the NiO(111) surface dosed by formic acid are shown in Figure 3. The surface was exposed to the saturation coverage of formic acid at 163 K, and the sample was subsequently heated to the stated temperatures. Peaks were observed at 2860, 1570, 1360, and 778 cm^{-1} and are assigned to the C–H stretching, asymmetric O–C–O stretching, symmetric O–C–O stretching, and in-plane deformation modes, respectively, of bidentate formate.¹⁰ The appearance of the band of the O–C–O asymmetric stretching mode indicates that the formate molecules inclined on the surface. The peak at 2947 cm^{-1} was possibly due to the C–H stretching mode of the physisorbed formic acid molecule which disappeared around 273–323 K. The intensities of the formate peaks decreased at higher temperature as formate

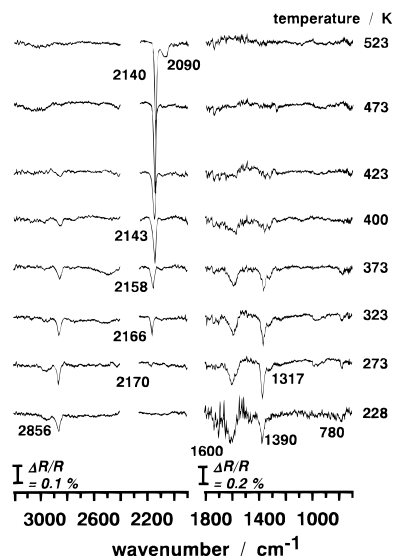


Figure 4. IRA spectra of formate (HCOO) and CO coadsorbed on NiO(111). The formate-covered NiO(111) was first heated to the stated temperatures for a few minutes in a vacuum. Then, the CO adsorption to the saturation coverage and the spectral measurement were carried out at 100 K.

decomposed. The band of the symmetric O—C—O stretching mode at 1360 cm^{-1} disappeared at 373 K, but its shoulder peak at 1317 cm^{-1} remained until 473 K, indicating that the formate species giving the peaks at 1360 and 1317 cm^{-1} decomposed at 340–390 and 520 K in the TPD measurement, respectively. It is hard to discuss the differences in structures and adsorption sites of the two kinds of formate from frequencies of the symmetric O—C—O stretching mode alone, and we proceeded to use CO as the probe of the adsorption sites of formate.

Shown in Figure 4 are the IRA spectra observed after the CO adsorption of the formate-covered NiO(111); the surface was heated to the stated temperatures for a few minutes in a vacuum, cooled to 100 K, and dosed by CO to the saturation coverage. The behavior of the formate peaks at 2860, 1570, 1360, and 778 cm^{-1} in Figure 4 is similar to that in Figure 3, suggesting that the adsorbed CO does not affect the structure and decomposition of the remaining formate. The changes in the area intensities of the formate and CO bands by the heated temperatures are displayed in Figure 5. The surface heated at 228 K was solely covered by formate to the saturation coverage, and CO molecules did not adsorb. The IRAS bands of the CO appeared for surfaces annealed at and above 273 K. The intensity of the band at 2170 cm^{-1} coming from CO on the HF sites increased by increasing the annealing temperature. The band at 2090 cm^{-1} corresponding to the adsorbed CO on the LF sites gained the intensity when the surface was heated to 523 K. It must be noted that the frequency of adsorbed CO on the HF sites obtained from the formate covered surface around 300 K is 17 cm^{-1} higher than that on clean NiO(111) when the CO coverage was small. This difference in frequency is considered to be due to interaction between CO and formate. Formate on a surface is regarded as an anionic species, and the shift to higher frequency of coadsorbed CO may be caused by withdrawing of the surface electrons to lessen the back-donation to the $2\pi^*$ state of CO by formate species.^{19,20}

The arrows a and b in Figure 5 indicate the area intensities of the bands by CO adsorbed on the HF and LF sites, respectively, of the initial NiO(111) surface before the adsorption of formic acid. The desorption peaks of the CO on the HF sites. It should be noted that the peak of CO on the HF

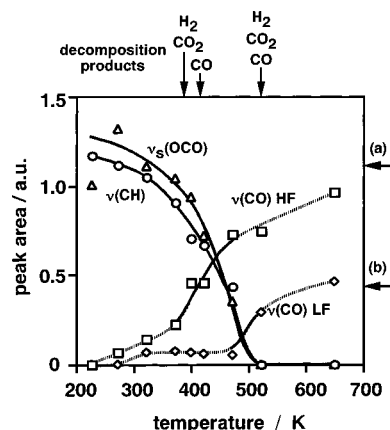


Figure 5. Temperature dependence of the area intensities of the vibrational peaks of formate and CO. The areas were derived from the spectra shown in Figure 4. The arrows a and b indicate the area intensities of the band by the CO adsorbed on HF and LF sites, respectively, of the initial surface without the adsorption of formic acid. The desorption peaks of the TPD signals are indicated on the top.

sites drastically gained intensity around 400 K but that on the LF sites gained around 500 K. When the formate-covered surface was heated to 650 K, the CO peaks recovered their initial intensities, indicating that the surface structure was recovered. The feature suggests that the decomposition of formate at 340–415 K took place mainly on the HF sites since CO started to adsorb on the HF sites at this temperature. The decomposition of formate at 520 K, on the other hand, occurred at LF sites. It is thus concluded that the decomposition of formate on the fully-oxidized Ni cation sites on the terraces gave 340–415 K peaks on the TPD signals and those on the less-oxidized Ni sites at 520 K.

Behavior of Hydroxyl Species (—OD). It is important to note the role of the surface hydroxyl species during the decomposition of formate since a product of water should be originated from the surface hydroxyl species. The behavior of hydroxyl species during the decomposition of formate has not been understood because of the low sensitivity of hydroxyl species for IRAS. Moreover, the difficulty of the detection of water in TPD also interfered with understanding the reaction path of the water production. The use of deuterated formic acid DCOOD enables us to detect the surface hydroxyl species on IRAS by taking advantage of a much better signal-to-noise ratio in the O—D stretching region ($\sim 2700\text{ cm}^{-1}$) than that in the O—H stretching region ($\sim 3700\text{ cm}^{-1}$).

Hydroxyl species on NiO(111) were examined first without adsorption of formic acid. IRA spectra of surface hydroxyl species obtained from the dissociative adsorption of heavy water D_2O at the stated temperatures on NiO(111) are shown in Figure 6. At the low adsorption temperature of 163 K, two peaks were observed at 2709 and 2624 cm^{-1} which are assigned to the O—D stretching modes of the dangling and hydrogen-bonded OD groups, respectively, of the adsorbed D_2O molecule. In the temperature region between 228 and 550 K, a single peak was observed at $2709\text{--}2719\text{ cm}^{-1}$ and is assigned to the O—D stretching mode of the hydroxyl species.^{21,22} The peak position shifted from 2719 to 2709 cm^{-1} on increasing the substrate temperature from 228 to 550 K and might be due to the anharmonic coupling with low-frequency modes such as the frustrated translation of the hydroxyl groups as suggested for the CO on metal surfaces.²³ The frequency of this peak suggests that the hydroxyl species do not interact with each other through hydrogen bonding. The peak of the hydroxyl species disappeared at 650 K. Spectrum a was obtained after the surface

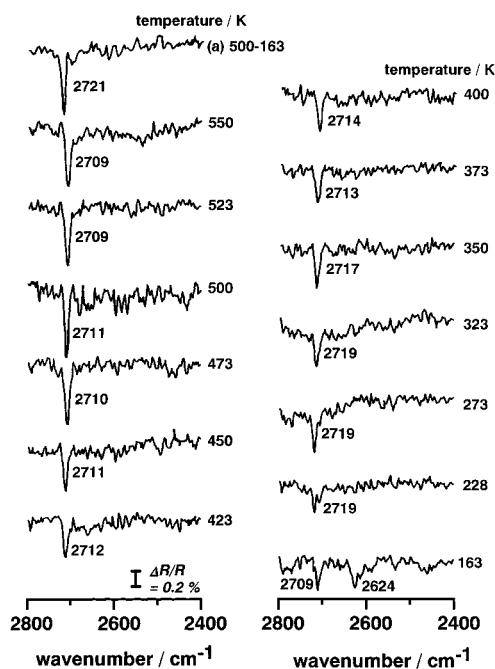


Figure 6. IRA spectra of NiO(111) exposed to 10 langmuirs of D₂O at the stated temperatures. Spectrum a was obtained after the surface was dosed by D₂O at 500 K and cooled to 163 K.

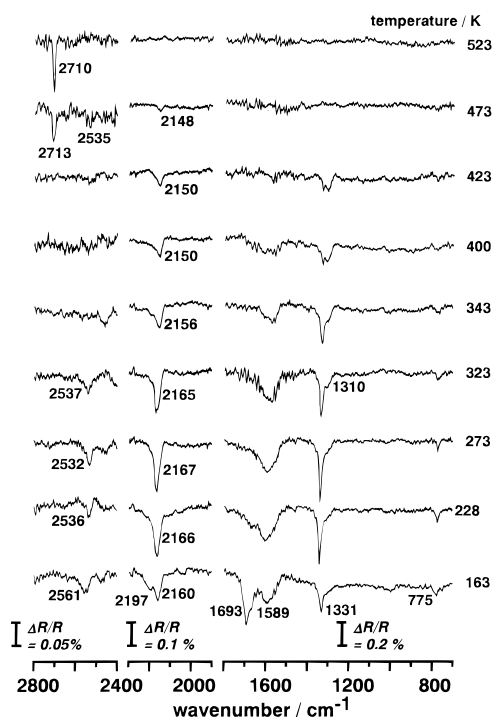


Figure 7. Temperature-dependent IRA spectra of formate (DCOO⁻) adsorbed on NiO(111). The surface was exposed to DCOOD (10 langmuirs) at 163 K and then heated to the stated temperatures.

was dosed by D₂O at 500 K and was cooled to 163 K. A single peak was observed at 2721 cm⁻¹. The frequency shift dependent on the substrate temperature indicates that this peak is assigned to the band of isolated hydroxyl species.

The behavior of surface hydroxyl species produced by the decomposition of formic acid was different from that produced by the adsorption of water. Figure 7 shows IRA spectra of the NiO(111) surface dosed by deuterated formic acid DCOOD in the same way as that of Figure 2. The peaks at 2160, 1589, 1331, and 775 cm⁻¹ were assigned to the C–D stretching, antisymmetric O–C–O stretching, symmetric O–C–O stretch-

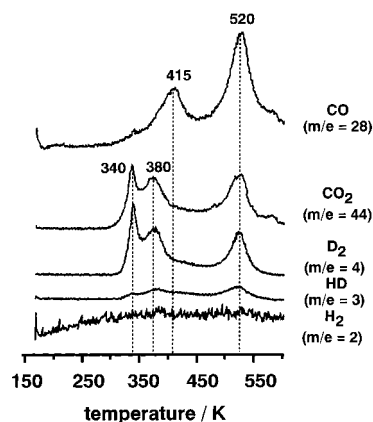


Figure 8. TPD spectra of the DCOOH dosed on the NiO(111) surface. The surface was exposed to 10 langmuirs of DCOOH at 163 K.

ing, and in-plane deformation modes of bidentate formate (DCOO⁻), respectively. A peak was observed at 2536 cm⁻¹ between 228 and 323 K and is assigned to the O–D stretching mode of surface hydroxyl species produced by the dissociation of formic acid to formate. The frequency of 2536 cm⁻¹ is by 180 cm⁻¹ lower than that of the isolated hydroxyl species from D₂O. This indicates that the present hydroxyl species was perturbed by the coadsorption of formate through either the hydrogen bonding or electronic change of the adsorption site by the adsorption of anionic formate on the neighboring sites. The hydroxyl peak disappeared above 323 K, and the hydroxyl species possibly desorbed at this temperature as D₂O. In conclusion, we considered that a part of water is produced and desorbs below 343 K by the decomposition of formic acid.

When the surface temperature was raised to 473 K, a new peak appeared at 2713 cm⁻¹ and was also assigned to the O–D stretching mode of the hydroxyl species. The frequency of the band is the same as that of the hydroxyl species formed from D₂O, indicating that these hydroxyl species are isolated. This type of hydroxyl species is considerably produced by the decomposition of the formate remaining at higher temperature to give the symmetric O–C–O stretching band at 1317 cm⁻¹. Although the TPD signal of water could not be detected, the IRA spectra clearly proves that there are two origins for the desorption of water by the decomposition of formic acid: one from the formate-perturbed hydroxyl species around 343 K and the other from isolated hydroxyl species around 650 K.

TPD spectra of the DCOOH-dosed surface were measured to reveal which hydrogen in the formic acid is the source for the hydrogen and water production, as shown in Figure 8. The locations of TPD peaks of CO₂ and CO are almost the same as those observed for the HCOOH-dosed surface. It is seen that D₂ was produced from DCOOH but the signals of H₂ or HD were hardly observable. It clearly indicates that the hydroxyl species produced at the oxygen sites on dissociative adsorption of formic acid desorbed primarily as water but not as hydrogen. It is thus reconfirmed that the disappearance of the IRAS peaks of the hydroxyl species is due to the desorption as water.

Desorption at 343 K of water produced from hydroxyl groups should leave behind an oxygen vacancy. However, the AES ratio of the O/Ni signals remained unchanged after several repetitions of TPD, and the thus created vacancies were apparently recovered by the oxygen atoms supplied by the further decomposition of formate. As a matter of fact, the change by the desorption of the hydroxyl species was not observed in the CO-probe measurements, suggesting that the CO does not adsorb on the oxygen-vacancy sites generated from

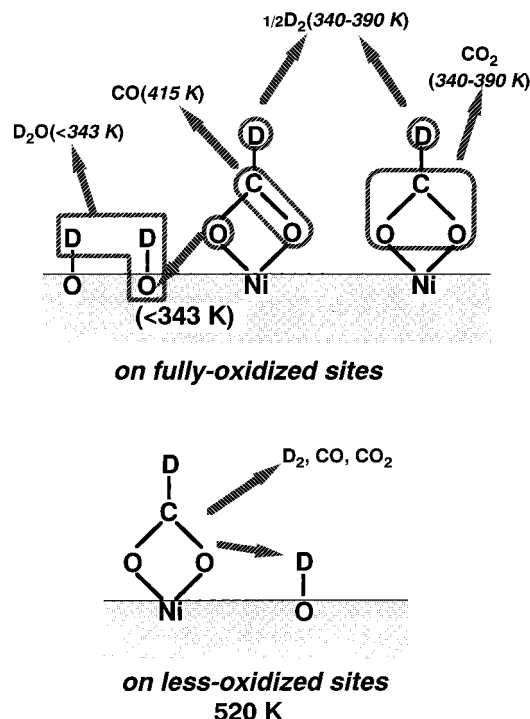


Figure 9. Schematic model for the decomposition of formic acid on NiO(111).

the desorption of water due possibly to the morphology of the sites or blocking by the nearest formate species. We propose the scheme for the decomposition reaction as displayed in Figure 9.

Adsorption of Formic Acid on Hydroxyl-Covered NiO(111). Next investigated was the adsorption of formic acid on the NiO(111) surface which was precovered by the D₂O-originated OD groups. The surface was prepared by exposure to the 10 langmuirs of D₂O vapor at 500 K. This hydroxylation condition is known to produce the largest amount of the isolated hydroxyl species on NiO(111) and disrupt the (2 × 2) microfacets.⁵ Figure 10 shows IRA spectra of formic acid adsorbed on hydroxylated NiO(111) as a function of temperature, where the shown spectra are the ratio spectra divided by those of hydroxylated NiO(111). When the surface was dosed at 163 K, a large reduction of the peak intensity, that is the negative peak on the ratio spectra, was observed at 2711 cm⁻¹, and a peak appeared at 2534 cm⁻¹ which was assigned to the hydroxyl species perturbed by formate. The intensity of the 2534 cm⁻¹ peak was almost twice that observed on clean NiO(111). The feature suggests that the isolated hydroxyl species initially produced on the preparation transformed its structure to the hydroxyl species perturbed by formate. This peak disappeared around 323 K as was the case on clean NiO(111), confirming that the formate-affected hydroxyl species desorbs around 323 K irrespective of their origin. At the temperature higher than 473 K, the negative peak at 2711 cm⁻¹ disappeared, indicating that the isolated hydroxyl species was recovered by decomposition of formic acid.

The temperature-dependent change of the formate peaks on hydroxylated NiO(111) was not different from that on the clean NiO(111). The intensity ratio of the antisymmetric and symmetric O—C—O stretching bands varies by the tilt angle of formate from the surface normal, and the invariance suggests that the tilt angle on hydroxylated NiO(111) was the same as that on clean NiO(111). The formate stood vertical to the surface in the condition of the steady-state reaction under a continuous flow of formic acid.¹³

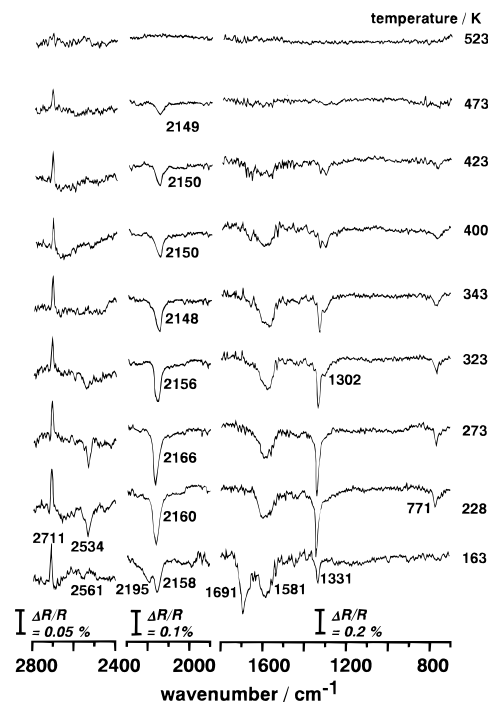


Figure 10. Temperature dependence of IRA spectra of formate adsorbed on hydroxyl (—OD)—precovered NiO(111). The surface was exposed to 10 langmuirs of D₂O at 500 K to produce isolated hydroxyl species. The hydroxyl-covered NiO(111) was then exposed to the 10 langmuirs of DCOOD at 163 K and then heated to the stated temperatures. All spectra were normalized against the spectrum of the initial hydroxyl-covered NiO(111) at 500 K.

Conclusion

The findings are summarized as follows.

(1) There are two decomposition temperatures, 340–415 and 520 K, for the formate on NiO(111). The frequency of the CO adsorbed on the partially decomposed surface indicated that the decompositions at 340–415 and 520 K took place on the fully-oxidized Ni cation sites and the less-oxidized Ni cation sites, respectively.

(2) The IRAS peaks of surface hydroxyl species (OD) examined during formate decomposition on clean and hydroxylated NiO(111) revealed that the 2530 cm⁻¹ peak of the hydroxyl species interacting with formate disappeared around 323 K, indicating that the hydroxyl species desorbs as water. On heating the substrate to 473 K, the isolated hydroxyl species was formed from the decomposition of formate, giving the peak at 2711 cm⁻¹. It desorbed at 650 K with further heating.

References and Notes

- (1) Henrich, V. E.; Cox, P. A. *The Surface Science of Metal Oxides*, 1st ed.; Cambridge University Press: New York, 1994; Chapter 1.
- (2) Kuhlbeck, H.; Odörfer, G.; Jaeger, R.; Illing, G.; Menges, M.; Mull, Th.; Freund, H.-J.; Pohlchen, M.; Staemmler, V.; Witzel, S.; Scharfshwerdt, C.; Wennemann, K.; Liedtke, T.; Neumann, M. *Phys. Rev. B* **1991**, 43, 1969.
- (3) Wulser, K.; Langell, M. A. *Catal. Lett.* **1992**, 15, 39.
- (4) Troung, C. M.; Wu, M. C.; Goodman, D. W. *J. Phys. Chem.* **1992**, 97, 9447.
- (5) Rohr, F.; Wirth, K.; Libuda, J.; Cappus, D.; Bäumer, M.; Freund, H.-J. *Surf. Sci.* **1994**, 315, L977.
- (6) Ventrice, C. A.; Bertrams, Th.; Hannemann, H.; Brodde, A.; Neddermeyer, H. *Phys. Rev.* **1994**, B49, 5773.
- (7) Xu, C.; Goodman, D. W. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 3709.
- (8) Xu, C.; Goodman, D. W. *Catal. Today* **1996**, 28, 297.
- (9) Schönnenbeck, M.; Cappus, D.; Klinkmann, J.; Freund, H.-J.; Pettersson, L. G. M.; Bagus, P. S. *Surf. Sci.* **1996**, 347, 337.

- (10) Bandara, A.; Kubota, J.; Wada, A.; Domen, K.; Hirose, C. *Surf. Sci.* **1996**, *364*, L580.
- (11) Bandara, A.; Kubota, J.; Wada, A.; Domen, K.; Hirose, C. *J. Phys. Chem.* **1996**, *100*, 14962.
- (12) Kubota, J.; Bandara, A.; Wada, A.; Domen, K.; Hirose, C. *Surf. Sci.* **1996**, *368*, 361.
- (13) Bandara, A.; Kubota, J.; Wada, A.; Domen, K.; Hirose, C. *J. Phys. Chem. B* **1997**, *101*, 361.
- (14) Henderson, M. A. *J. Phys. Chem.* **1995**, *99*, 12919.
- (15) Wu, M.-C.; Goodman, D. W. *Catal. Lett.* **1992**, *15*, 1.
- (16) Petrie, W. T.; Vohs, J. M. *Surf. Sci.* **1991**, *245*, 315.
- (17) Dilara, P. A.; Vohs, J. M. *J. Phys. Chem.* **1993**, *97*, 12919.
- (18) Yoshinobu, J.; Ballinger, T. H.; Xu, Z.; Jansch, H. J.; Zaki, M. I.; Xu, J.; Yates, J. T., Jr. *Surf. Sci.* **1991**, *225*, 295.
- (19) Zaki, M. A.; Knözinger, H. *J. Catal.* **1989**, *119*, 311.
- (20) Vesecky, S. M.; Xu, X.; Goodman, D. W. *J. Vac. Sci. Technol.* **1994**, *A12*, 2114.
- (21) Sanders, H. E.; Gardner, P.; King, D. A.; Morris, M. A. *Surf. Sci.* **1994**, *304*, 159.
- (22) Kondo, J. N.; Yuzawa, T.; Kubota, J.; Domen, K.; Hirose, C. *Surf. Sci.* **1995**, *343*, 71.
- (23) Clark, R. J. H.; Hester, R. E. *Spectroscopy of Surfaces*; John Wiley & Sons, Ltd: New York, 1988; Chapter 8.