Formation of Formate in the Deep Oxidation of Methanol on Pt(111) under UHV Condition Studied by IRAS

Makoto Endo, Taketoshi Matsumoto, Jun Kubota, Kazunari Domen, and Chiaki Hirose*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

The reaction of methanol with oxygen on Pt(111) under ultrahigh vacuum condition has been investigated by infrared reflection absorption spectroscopy (IRAS). Molecular and atomic states of adsorbed oxygen existed on the Pt(111) surface, and the adsorption of oxygen at 100 K gave molecularly adsorbed oxygen that dissociated to adatoms at ∼160 K. Formate species, which gave the symmetric C−O stretching band at 1327 cm^{-1}, was observed when methanol-adsorbed Pt(111) surface, which was precovered by molecular oxygen, was heated to 160 K. The IRAS band of formate was verified by comparison with the band of the formate derived from formic acid on the Pt(111) surface and by the isotope shift of the band observed by using deuterated methanol. The amount of produced formate was proportional to the amount of the molecularly adsorbed oxygen. The formate band disappeared at 270 K, at which temperature desorption of CO_2 and H_2 was observed on temperature-programmed desorption spectra. Molecular oxygen on the Pt(111) surface dissociated at 300 K and the produced adatoms did not oxidize methanol, but the methanol was decomposed to CO and H_2. Molecularly adsorbed oxygen is thus considered to be responsible for the oxidation of methanol to formate.

Introduction

Oxidation of molecules on metal surfaces is the subject that leads to the understanding of the reactions in such systems as catalytic combustion, automotive emission control, partial oxidation, and fuel cells.[1−3] The investigation of the mechanism of methanol oxidation specifically has been performed with prime interest in the partial oxidation to formaldehyde on such surfaces as copper, silver, and platinum.[4−10] On the other hand, the mechanism of deep oxidation of methanol, which produces CO_2 instead of formaldehyde, has not been investigated that well. As a matter of fact, the oxidation of methanol on the Pt(111) surface has been investigated only on the surface that is adsorbed by atomic oxygen, although molecular oxygen also adsorbs at the temperature below 150 K. It has been reported that methanol is transformed, by the preadsorbed oxygen atoms, to methoxy species on the Pt(111) surface with the formation of H_2O,[11−14] and Akhter and White reported that CO_2 is produced only when methanol is thinly adsorbed on the atomic-oxygen-covered Pt(111) surface.[12] They suggested that the produced methoxy species decomposes to CO and H_2, and a small part of the products is oxidized to CO_2 and H_2O by oxygen adatoms, that is, the key factor in the deep oxidation of methanol on platinum surfaces is the oxidation of adsorbed CO in the step that follows the production of CO from methoxy species. The investigation on the surface that is covered by molecular oxygen has been lacking.

The adsorption of oxygen on Pt(111) is now well established; molecular adsorption takes place at the temperature below 150 K, and a part of the adsorbed oxygen molecules desorbs and the other part dissociates at around 150 K.[16,17] The dissociated oxygen atoms recombine and desorb at ∼700 K. When the oxidation of molecules on such a surface is considered, one

pictures that the oxygen molecules dissociatively adsorb on the surface and the generated adatoms oxidize reactant molecules.[1−3] It has been reported, however, that the molecularly adsorbed oxygen is the species that promotes the oxidation of CO,[18,19] NH_3,[20] and HCN.[21] The reactivity of adsorbed oxygen molecules was also suggested for the isotope exchange reaction in the NO/Pt(111) system.[22] As such, there arises a question of whether the high reactivity of molecularly adsorbed oxygen on the Pt(111) surface, explained by either hot atom mechanism[20] or peroxo complex[21] mechanism, is also operative in the oxidation of methanol. In this study, a detailed investigation of the roles of molecularly and atomically adsorbed oxygens in the oxidation of methanol was carried out to get an understanding of the detailed mechanism of the oxidation reaction.

We have already reported on the infrared reflection absorption spectroscopy (IRAS), which indicated that the oxidation of methanol to formate proceeds under the presence of molecularly adsorbed oxygen.[15] We identified the IRAS band of formate on the Pt(111) surface subjected to the catalytic oxidation of methanol under the flow of methanol, oxygen, and helium mixture at atmospheric pressures, and the results suggested that the formation of formate is essential in the catalytic oxidation. In this article, a detailed account is given of the observation and interpretation for the formation of formate by molecularly adsorbed oxygen during the oxidation of methanol on the Pt(111) surface under ultrahigh vacuum (UHV) condition.

Experimental Section

Experiments were performed in a UHV system (base pressure of ∼10^{-8} Pa) composed of sample preparation and IRAS chambers.[15,23] The preparation chamber was equipped with an Ar ion gun, an Auger electron spectroscopy and low-energy electron diffraction composite analyzer, and a quadrupole mass

spectrometer (QMS). Temperature-programmed desorption (TPD) spectra were measured by the QMS. The IRAS chamber was equipped with two BaF_2 windows for the introduction and extraction of infrared beam and a leak valve for the introduction of sample gases. The amounts of dosage of CH_3OH and O_2, denoted by L ($1\ L = 1 \times 10^{-6}$ Torr s, 1 Torr = 133 Pa), were derived from the apparent pressures measured by an ionization gauge.

The Pt(111) sample (10 mm in diameter and 1 mm thick) was mounted onto the tip of a liquid-nitrogen-cooled sample holder by two Ta wires (0.3 mm in diameter). The wires were spot-welded to the backface of the sample piece. The sample temperature was controlled by the resistive heating of the Ta wires and measured by a thermocouple spot-welded to the sample piece. The sample surface was prepared by cycles of Ar$^+$ bombardment at 700 K and annealing at 1100 K. The CH_3OH sample was purified by repeated freeze−pump−thaw cycles, and commercial O_2 gas (99.999% purity) was used without purification.
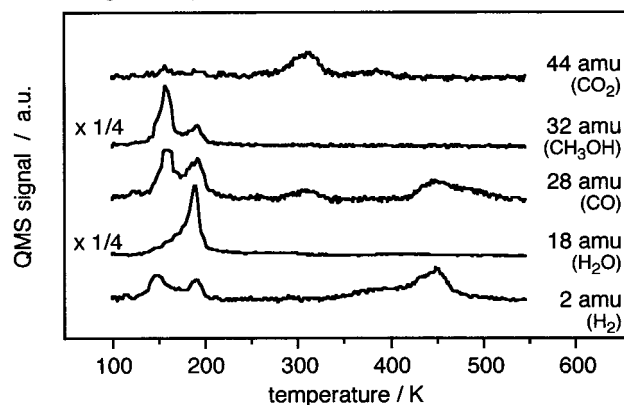
IRA spectra at 4 cm^{-1} resolution were obtained by a JEOL JIR-100 Fourier transform infrared spectrometer with a HgCdTe detector (Graseby-Infrared, FTIR-N13). A wire grid polarizer, which was revolved by a stepping motor, was used to obtain the ratio spectra for the p- and s-polarized beams to cancel out the absorption by water vapor and CO_2 in the atmosphere.

Results and Discussion

Reactions on three kinds of oxygen-precovered Pt(111) surfaces were investigated. The surface covered solely by molecular oxygen [denoted as the O_2/Pt(111) surface hereafter] was prepared by the exposure of oxygen at 100 K, and the surface covered only by atomic oxygen [denoted as the O/Pt(111) surface hereafter] was prepared by annealing the molecule-precovered surface at 300 K.[16,17] The preparation of the surface that was coadsorbed by molecular and atomic oxygens is described later. Most of oxygen adsorbates are molecular when dosed at 100 K, and the molecules dissociate to atoms at around 160 K with the desorption of excess molecules. The surface saturated by atomic oxygen is known to form a (2 × 2) structure at 300 K and the absolute coverage is 0.25 with respect to the number of surface Pt atoms.[16,17] The atomic oxygen recombinatively desorbed around 700 K. As described later, the amounts of O_2 from molecularly adsorbed oxygen is three times higher than that from atomically adsorbed oxygen, indicating that the coverage of oxygen molecules before dissociation is 0.5, that is, the number of O_2 molecules on the O_2/Pt(111) surface is twice that of the O atoms on the O/Pt(111) surface.

TPD Measurements. The TPD spectra observed after adsorbing CH_3OH onto the O_2/Pt(111) and O/Pt(111) surfaces are shown in Figure 1. The adsorption of CH_3OH was carried out at 100 K. The results from the O_2/Pt(111) surface is shown in Figure 1a; observed signals of the parent methanol at 32 amu (atomic mass unit) and its cracking products at 28 and 2 amu indicate that multilayered CH_3OH desorbed at 155 K. The signals at 180 K indicate that a part of the CH_3OH in the first layer desorbed molecularly at this temperature. The desorption of H_2O (18 amu) took place at the same temperature. With further heating of the surface, CO_2 desorbed at 300 K and the desorption of H_2 and CO took place at around 420 K. The estimated quantities of the desorbed CO_2 and CO were the same, indicating that only half of the adsorbed CH_3OH was oxidized to CO_2 by molecular oxygen. The results from the O/Pt(111)
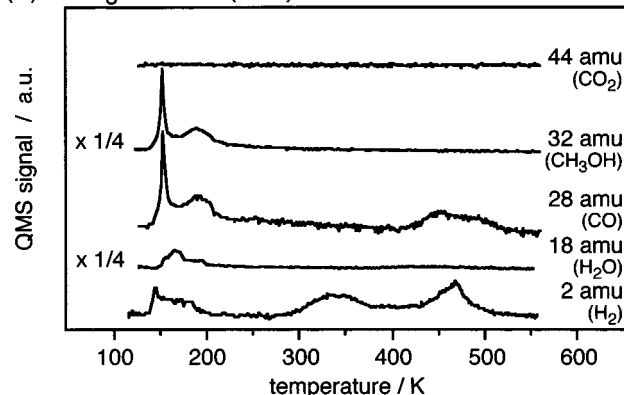

Figure 1. TPD spectra of the oxygen-precovered and methanol-dosed Pt(111) surfaces. The results for O_2/Pt(111) and O/Pt(111) are shown in (a) and (b), respectively. The surface for (a) was prepared by the exposure of excess amounts of oxygen (20 L) at 100 K to ensure saturation coverage, and that for (b) was prepared by annealing O_2/Pt(111) at 300 K. Methanol was introduced by 1-L exposure to give multilayer deposition.
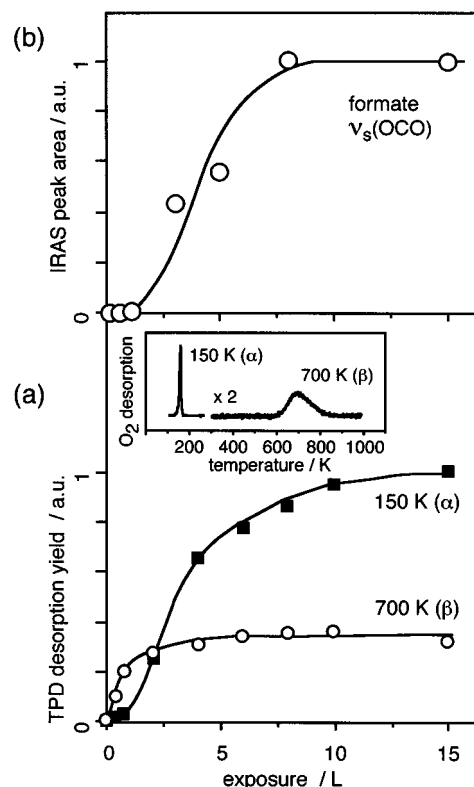
surface is shown in Figure 1b; CH_3OH decomposed to H_2, CO, and H_2O at similar temperatures observed on the O_2/Pt(111) surface. However, no desorption of CO_2 was observed this time and the amount of desorbed H_2O was very small. This desorption feature is in good agreement with the results reported previously.[11] As considerable amounts of H_2O and CO_2 were produced only on the O_2/Pt(111) surface, we interpreted that the molecularly adsorbed oxygen was responsible for the deep oxidation of methanol on the Pt(111) surface.

Interaction of Methanol with Molecularly Adsorbed Oxygen by IRAS. IRAS measurements were performed to get further information on the mechanism of the oxidation of methanol to CO_2. Shown in Figure 2 are the spectra observed at various temperatures for the surface that was prepared by adsorbing CH_3OH onto O_2/Pt(111) at 100 K. No distinct vibration band was observed in the ranges above 2200 cm^{-1} and between 1400 and 1900 cm^{-1}; we could not successfully detect the vibrational bands in the C−H stretching region because of small absorption coefficients. Observed after the dosing at 100 K are the peak at 1046 cm^{-1} with a shoulder at 1030 cm^{-1} and a broad band at 1127 cm^{-1}. The 1046 cm^{-1} peak is assigned to the C−O stretching band of CH_3OH in the multilayer, and the broad absorption band at 1127 cm^{-1} to the CH_3 rocking mode of adsorbed CH_3OH.[9,11,24,25] The shoulder band at 1030 cm^{-1} is possibly due to the CH_3OH in the first layer. These peaks disappeared and new peaks appeared at 1324 and 2086 cm^{-1} when the surface was heated to above 160 K.
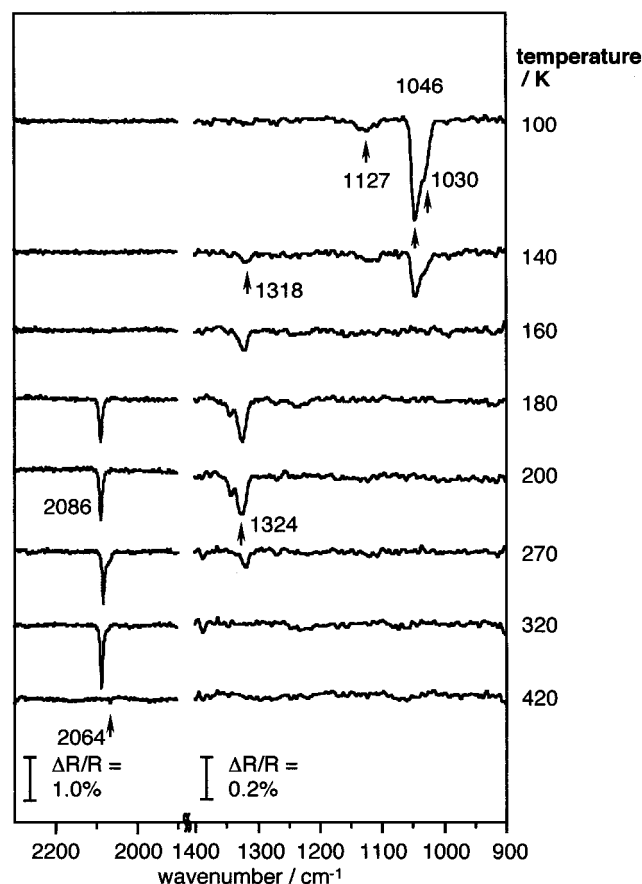
Figure 2. IRA spectra of CH₃OH adsorbed on O₂/Pt(111) that was prepared by exposure of excess amounts of oxygen at 100 K. CH₃OH was introduced by 1 *L* at 100 K and the spectra were measured after heating the sample to the stated temperatures.

Figure 3. Changes of area intensities of the oxygen α and β peaks of the TPD signals [(a), see text for the meaning of the two peaks] and the formate IRAS peak, observed at 200 K, (b), by the exposure of oxygen. The intensity of the IRA signal varied similarly to that of the α peak.

We assign the 1324 cm^{-1} peak to the C$-$O symmetric stretching mode of formate (HCOO),[26–29] which was produced by the oxidation of CH₃OH, and the 2086 cm^{-1} peak to the CO stretching band of CO adsorbed in on-top configuration,[9,30] produced by the decomposition. (Confirmations for the assignment of the 1324 cm^{-1} band to formate are described later.) Formate has the antisymmetric and symmetric C$-$O stretching modes in the1600~1800 and 1300~1400 cm^{-1} regions, respectively, with the frequencies and intensities dependent on the molecular structure (monodentate, bidentate, or bridging) and orientation (inclination).[31,32] The absence of the antisymmetric band on the observed spectra and the frequency of the C$-$O symmetric stretching band indicate that the observed formate adsorbed vertical to the surface with the bridging configuration. As seen in Figure 1a, H₂O desorbed at 180 K, and this temperature coincides with the appearance temperature of the 1324 cm^{-1} peak on the IRA spectrum. The 1324 cm^{-1} peak weakened at higher temperature and disappeared at 320 K. This temperature coincides with the temperature at which desorption of CO₂ was observed on the TPD spectrum (Figure 1a), suggesting that CO₂ was produced through a formate intermediate. (The desorption temperature of CO₂, 300 K, in the present work was somewhat higher than that in decomposition of formic acid reported in ref 25. We considered that the presence of CO from decomposition of CH₃OH affected the decomposition of formate.) At the same time, a part of CH₃OH decomposed at ~180 K to give adsorbed CO and H₂ as seen by the appearance of the CO band in the IRA spectra (Figure 2) and by the presence of ~450 K desorption peaks on the TPD spectra (Figure 1a).

We next examined the surface having various coverages of molecular oxygen by TPD and IRA spectra after various exposures to oxygen at 100 K. As already described, the O₂/Pt(111) surface is known to give two oxygen desorption peaks on TPD spectra: a peak at ~150 K (α peak) due to the desorption of molecular oxygen and a peak at ~700 K (β peak) due to the recombinative desorption of the adsorbed atomic oxygen produced by the dissociation of remaining molecules at around 150 K.[16,17] A typical spectrum observed for the saturation-covered surface is depicted in the inset of Figure 3a. Plotted in Figure 3a are the area intensities of the α peak (filled squares) and the β peak (unfilled circles) against the exposure of the surface to oxygen gas. One notes that the exposure of ~1 *L* is needed for the appearance of the α peak, whereas the β peak appears from the beginning.

The IRAS measurement was made after dosing methanol to the above-prepared surfaces by methanol at 100 K and heating the surface to 200 K. Figure 3b is the plot of the area intensities of the formate C$-$O peak against the oxygen exposures. One notices a close resemblance between the plot in Figure 3b and the plot of the α peak in Figure 3a in that both signals appeared after the preexposure of the surface exceeded 1 *L*. This resemblance presents us with more evidence that the molecular oxygen was responsible for the oxidation of methanol to formate.
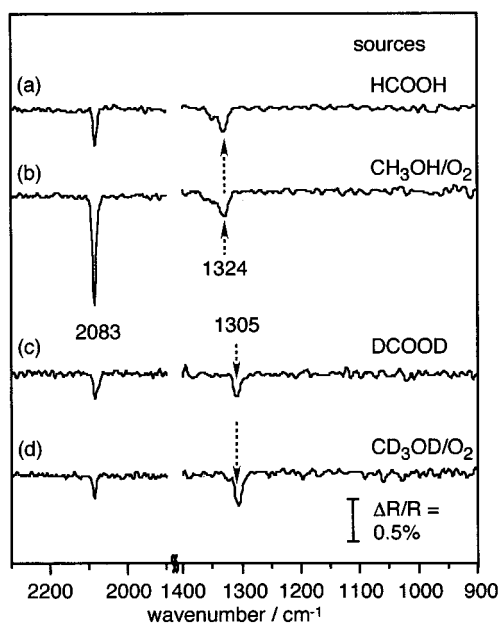
Figure 4 shows the IRA spectra observed at various temperatures after the adsorption of CD₃OD on the O₂/Pt(111) surface at 100 K. The spectra of the surface at 110 K gave the peaks of multilayered CD₃OD at 2214, 2071, 1127, and 981 cm^{-1} that were assigned to the degenerate and symmetric C$-$D stretching, CD₃ rocking, and C$-$O stretching modes of CD₃OD, respectively.[33] On raising the surface temperature, the peaks due to CD₃OD disappeared at 170 K and new peaks appeared at 1305

Formate Formation

J. Phys. Chem. B, Vol. 104, No. 20, 2000 **4919**
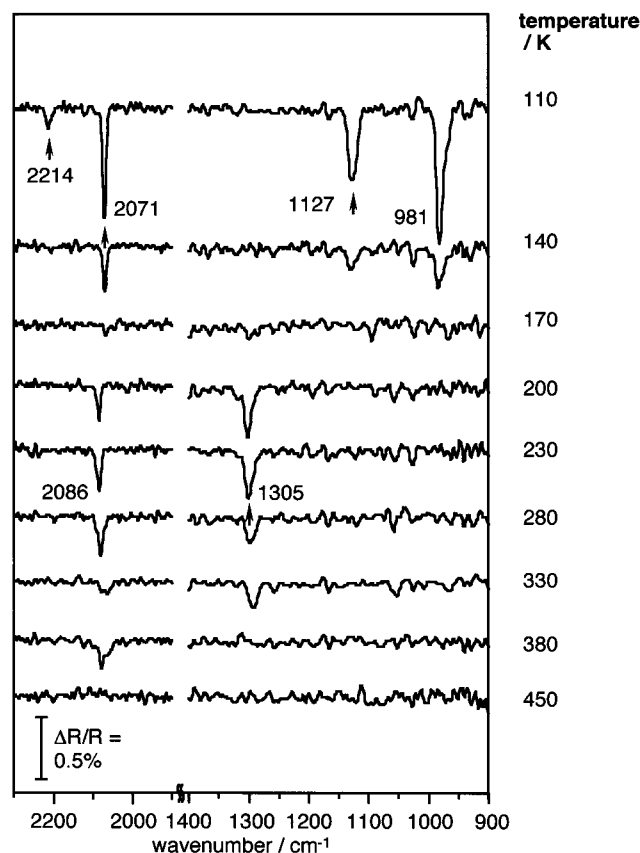
Figure 4. IRA spectra of CD₃OD adsorbed on O₂/Pt(111), which was prepared by exposure to oxygen at 100 K. CD₃OD was introduced by 1 *L* at 100 K and the spectra were measured after heating the sample to the stated temperatures.


Figure 5. Comparison of IRA spectra of formate produced by the adsorption of formic acid onto Pt(111) and the spectra observed on the surface subjected to oxidation of methanol. Traces (a) and (c) are the IRA spectra of the HCOOH- and DCOOD-adsorbed Pt(111) surfaces, respectively, and (b) and (d) are the spectra observed after heating to 200 K the CH₃OH- and CD₃OD-adsorbed O₂/Pt(111), prepared at 100 K, respectively. HCOOH and DCOOD were introduced to Pt(111) at 200 K and spectra were recorded at 200 K. All surfaces were under saturation coverage.

and 2086 cm⁻¹ at the temperature around 170−200 K. The new peak at 1305 cm⁻¹ is shifted by 19 cm⁻¹ from the corresponding peak observed on the CH₃OH-adsorbed surface, and the magnitude is in agreement with the value reported as the isotope shift for the C−O symmetric stretching band of formate in a previous work.[34] Our assignment of the 1305 cm⁻¹ band to formate is thus supported. (Further substantiation of the assignment is presented in the next subsection.) The DCOO peak disappeared at 330 K. The behavior of the 2086 cm⁻¹ peak closely resembles that in the measurement made by using CH₃OH (Figure 2), and the peak is ascribed to CO produced by the decomposition of CD₃OD. The decomposition of DCOO to CO₂ took place at about 330 K, which is slightly higher than the temperature, 270 K, at which HCOO decomposed, and this difference is probably due to the kinetic isotope effect because the decomposition of formate generally follows primary kinetic isotope effect.[35,36]

Comparison with IRAS of Formate Derived from Formic Acid. The confirmation for the assignment of the ∼1300 cm⁻¹ peak to formate was provided by the IRA spectra measured after dosing formic acid on Pt(111) to produce formate by the dissociative adsorption. The IRA spectra observed for the HCOOH/Pt(111), CH₃OH/O₂/Pt(111), DCOOD/Pt(111), and CD₃OD/O₂/Pt(111) surfaces are shown by traces (a), (b), (c), and (d) in Figure 5, respectively. CH₃OH and CD₃OD were introduced onto the O₂/Pt(111) surface at 100 K and spectra were observed after the surface was gradually heated to 200 K. HCOOH and DCOOD were dosed onto the Pt(111) surface at 200 K. The peaks at 1324 cm⁻¹ in (a) and 1305 cm⁻¹ in (c) have been assigned to the symmetric C−O stretching mode of formate,[26−29] and the peak around 2083 cm⁻¹ seen on all the

traces is presumably due to CO contamination. We find that the spectra observed for the methanol-treated surfaces, traces (b) and (d), are identical to those observed for the formic acid-dosed surfaces, traces (a) and (c). The assignment of the 1324 and 1305 cm⁻¹ peaks to formate is thus established. Furthermore, similar intensities of the 1324 cm⁻¹ peak between traces (a) and (b) and those of the 1305 cm⁻¹ peak between traces (c) and (d) indicate that the amount of the formate produced by the methanol oxidation on the O₂/Pt(111) surface was comparable with that produced from the dissociation of formic acid on the Pt(111) surface.

Interaction of Methanol with Atomically Adsorbed Oxygen by IRAS. Although the decomposition of methanol on the atom-precovered [O/Pt(111)] surface has been reported by several authors,[11−14] we also examined it to compare with the results on the molecule-precovered [O₂/Pt(111)] surface. As expected, the decomposition of methanol took place in a similar manner as already reported. Figure 6 shows the IRA spectra of the O/Pt(111) surface after exposing it to CH₃OH at 100 K and heating to various temperatures. As for the O₂/Pt(111) surface, two peaks were observed at 1045 and 1124 cm⁻¹ in the temperature region between 100 and 130 K, and the two peaks are ascribed to the vibration modes of CH₃OH. On heating the surface above 130 K, these two peaks disappeared and only the C−O stretching band of the CO molecule emerged at 2086 cm⁻¹, with its appearance and disappearance features closely resembling those observed on the O₂/Pt(111) surface. However, the formate peak did not appear. The spectra measured by using CD₃OD are shown in Figure 7, and the behavior of the spectra is similar to that in the CH₃OH system, including that the DCOO peak did not appear. Incidentally, the previous report on the results of high-resolution electron energy loss spectroscopy (HREELS) identified the C−O stretching band of methoxy species (CH₃O) at ∼1000 cm⁻¹,[11] and we expected to observe the C−O band on the IRA spectrum, too. We could not identify
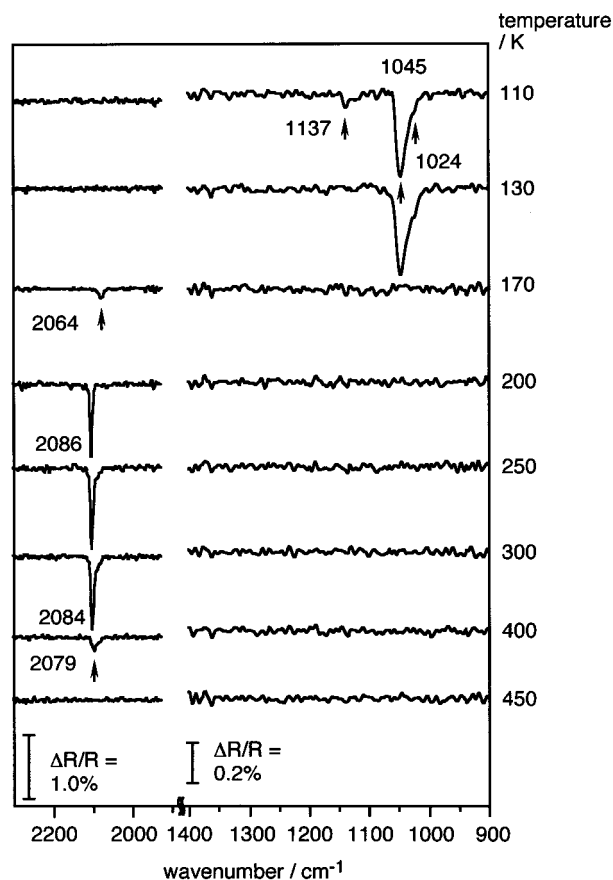
Figure 6. IRA spectra of CH_3OH adsorbed on O/Pt(111) that was prepared by annealing O_2/Pt(111) at 300 K to achieve the complete dissociation of oxygen molecules. CH_3OH was introduced by 1 *L* at 100 K and the spectra were measured after heating the sample to the stated temperatures.

Figure 7. IRA spectra of CD_3OD adsorbed on O/Pt(111), which was prepared by annealing the O_2/Pt(111) at 300 K. CD_3OD was introduced by 1 *L* at 100 K and the spectra were measured after heating the sample to the stated temperatures.

the band, however, and the failure arose presumably from the small number of methoxy molecules produced and lower sensitivity of IRAS compared with that of HREELS.

Combining the result by TPD with those obtained by IRAS for the CH_3OH and CD_3OD systems, it is postulated that methanol decomposed to adsorbed CO and H atoms at 170−200 K, and the two species desorbed at 450 and >300 K, respectively, as seen from the TPD spectra (Figure 1b). A part of the H_2O desorption signal seen in Figure 1b is probably ascribed to the occurrence of proton extraction by oxygen adatoms, which produced methoxy species from methanol.

IRAS of Methanol on Surfaces Coadsorbed by Molecular and Atomic Oxygens. The oxidation of methanol on the Pt(111) surfaces that were coadsorbed by molecular and atomic oxygens with various ratio was also examined. The studied surface was prepared in two steps. In the first step, the Pt(111) surface was subjected to prescribed dosing of oxygen at 100 K and was annealed at 300 K to make the surface under partial coverage by atomic oxygen. The thus-prepared surface was cooled to 100 K and exposed to oxygen with enough exposure this time so that molecular oxygen adsorbed to all the remaining adsorption sites.

We have shown that the area intensity of the α peak on the TPD spectrum of O_2 is proportional to the amount of the molecular oxygen on the surface, and the area intensities observed for the studied surfaces came out as shown in Figure 8a. Plotted in the figure are the area intensities of the α peak against the exposure taken in the first step of surface preparation, that is, the abscissa is the number of sites (in arbitrary units)
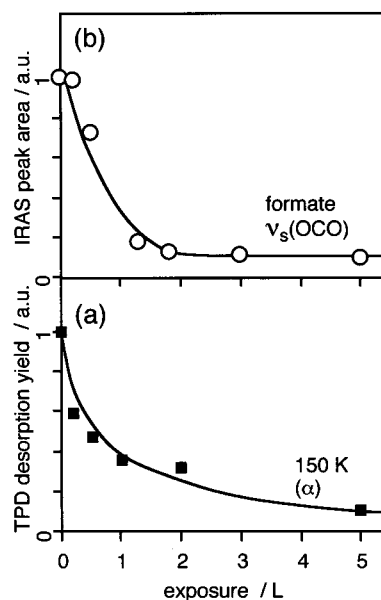
**Figure 8.** Changes of the area intensities of the α peak of the TPD signals [(a), see text for the meaning of the α peak] and the formate peak of the IRA spectra, observed at 200 K, (b) by the amount of atomic oxygen on the surface that was coadsorbed by molecular and atomic oxygens. See text for the preparation of the coadsorbed surfaces. Note that the surface was reexposed to oxygen at 100 K to the saturation coverage.

that are occupied by atomic oxygen. One sees that the amount of molecular oxygen decreased as the adsorption sites occupied by atomic oxygen increased. The feature applies to the surface at less than 1 *L* exposure, and a comparison with the feature

Formate Formation

J. Phys. Chem. B, Vol. 104, No. 20, 2000 **4921**
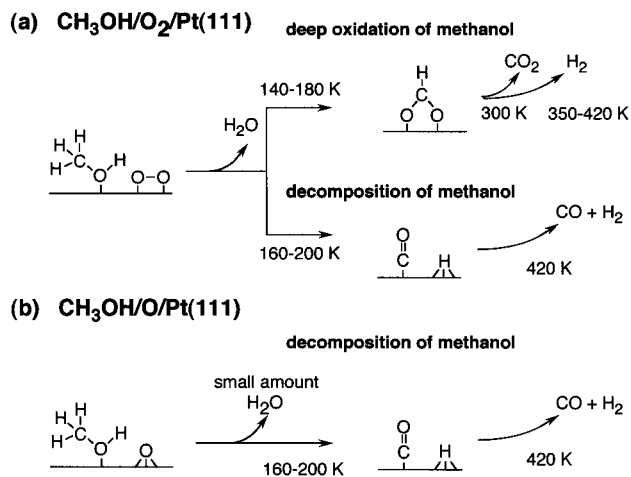
Figure 9. Conceivable reaction pathways for the deep oxidation and decomposition of methanol on $O_2/Pt(111)$ (a) and $O/Pt(111)$ (b).

shown in Figure 3 suggests that the annealing process killed the initially existing decomposition sites that produce oxygen atoms.

The area intensity of the 1324 cm^{-1} peak on the IRA spectra is proportional to the amount of the adsorbed formate. We thus measured the IRA spectra of the coadsorbed surfaces after dosing by methanol at 100 K and raising the temperature to 200 K. The area intensities of the 1324 cm^{-1} peak on various surfaces gave the plot, plotted against the first-step exposure as in Figure 8a, as shown in Figure 8b. Here again the amount of the surface formate decreased as the amount of the oxygen adatoms increased, and formate was not formed on the surface that was saturated by oxygen adatoms by more than 4 *L* preexposure in the first step of the surface preparation because there was no room for molecular oxygen to adsorb. Close similarity between Figure 8a and b testifies that the amount of formate goes with the amount of molecular oxygen.

Mechanism of Methanol Oxidation. Results of the present observation are summarized by the schemes in Figure 9. On the $O_2/Pt(111)$ surface, half of the adsorbed methanol molecules are oxidized to formate and the remaining half decompose to CO and H, as shown in Figure 9a. The formate decomposes to CO_2 at higher temperature. The reaction on the $O/Pt(111)$ surface, on the other hand, resulted in the decomposition to give out CO and H, as shown in Figure 9b. The key to the oxidation of methanol to formate on the Pt(111) surface is thus the presence of molecular oxygen.

As already mentioned, higher reactivity of molecularly adsorbed oxygen than atomically adsorbed oxygen has been reported for the oxidation reactions of CO,[18,19] NH_3,[20] and HCN,[21] and for the oxygen-exchange reaction of NO,[22] on the Pt(111) surface. Clear evidence was provided by Matsushima, who, from the experiment performed on the surface coadsorbed by atomic and molecular oxygens and using isotopically labeled species, revealed that only molecularly adsorbed oxygen reacts with CO.[18] The reaction temperature of ~180 K, as observed in the present study, is in good agreement with that for the oxidation of CO, NH_3, and HCN, indicating that a common mechanism is operative in all of the reactions.

The higher reactivity of molecular oxygen has been explained by either hot atom mechanism[20] or peroxo intermediate mechanism.[21] The hot atom mechanism is based on the fact that the potential energy of adsorbed oxygen molecules is higher than that of atomic oxygen by 130~460 kJ/mol with the value dependent on the coverage.[16] Oxygen atoms right after dis-

sociation are expected to have a large amount of excess energy as suggested by the recent observation by scanning tunnel microscopy,[37] which revealed the correlation between the site of the parent oxygen molecule with the location and interatom distance of the oxygen atoms produced by the dissociation. The released energy will serve as the driving force for the subsequent reaction of the produced atom. One should expect that the number of oxygen atoms right at dissociation temperature is somewhat more than that at stabilized saturation. The formation of formate on the $O_2/Pt(111)$ surface at lower oxygen coverage was not observed in the present study. The excess oxygen atoms may be the species that react with methanol to form formate, because these excess oxygen atoms cannot be quenched to the stable state. There, excess atoms may be regarded as hot atoms. Incidentally, the presence of formate as the product of a side reaction in the partial oxidation of methanol to formaldehyde on copper surfaces has been reported for the dosage of oxygen/methanol mixture,[38,39] and the finding was explained as that oxygen hot atoms on the surface participated to the deep oxidation to formate.[37] The peroxo intermediate mechanism postulates that an oxygen molecule directly attaches to the reactant and the thus-formed peroxo intermediate dissociates to the final product.[21] Although our results alone are not sufficient to give unequivocal distinction as to whether methanol reacts with oxygen molecules after or before dissociation, the coincidence of the temperatures for dissociation of oxygen molecules with that for the formation of formate fits with the hot atom mechanism. It should be safe to postulate that higher potential energy of an adsorbed oxygen molecule is indispensable for the oxidation of methanol to formate.

We have already reported that the formate is present on the Pt(111) surface when the catalytic oxidation of methanol by oxygen proceeds under atmospheric pressure.[15] A detailed study of the catalytic deep oxidation of methanol on the Pt(111) surface under ordinary pressure will be reported in a forthcoming paper.

Conclusion

Adsorbed methanol was found to be oxidized in a vacuum to form formate on the Pt(111) surface by molecularly adsorbed oxygen at 160 K, where the molecule-preadsorbed [$O_2/Pt(111)$] surface was prepared by dosing oxygen at 100 K, whereas the methanol simply decomposed to CO and H_2 without formation of formate on the atom-preadsorbed [$O/Pt(111)$] surface. The amount of the produced formate was proportional to that of the molecularly adsorbed oxygen, and thus the molecularly adsorbed oxygen is postulated to work to oxidize methanol to formate. The results as a whole seem to conform with the hot atom mechanism rather than the peroxo intermediate mechanism. The verification of IRAS band to formate was made by comparison with the IRAS band of the formate derived from the formic acid and also by the isotope shift of the band of the species derived from deuterated methanol.

References and Notes

(1) Masel, R. I. *Principle of Adsorption and Reaction on Solid Surfaces*; John Wiley & Sons: New York, 1996; Chapter 6.

(2) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994; Chapter 7.

(3) Campbell, I. M. *Catalysis at Surfaces*; Chapman and Hall: London, 1988.

(4) Yagasaki, E.; Masel, R. I. *R. Soc. Spec. Rep. Catal.* **1994**.

(5) Barteau, M. A.; Madix, R. J. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1982; Volume 4, Chapter 4.

(6) Wachs, I. E.; Madix, R. J. *J. Catal.* **1978**, *53*, 208.

(7) Sexton, B. A. *Surf. Sci.* **1979**, *88*, 299.

(8) Wachs, I. E.; Madix, R. J. *Surf. Sci.* **1978**, *76*, 531.

(9) Wang, J.; DeAngelis, M. A.; Zaikos, D.; Setiadi, M.; Masel, R. I. *Surf. Sci.* **1994**, *318*, 307.

(10) Wang, J.; Masel, R. I. *Surf. Sci.* **1991**, *242*, 199.

(11) Sexton, B. A. *Surf. Sci.* **1981**, *102*, 271.

(12) Akhter, S.; White, J. M. *Surf. Sci.* **1986**, *167*, 101.

(13) Sexton, B. A.; Rendulic, K. D.; Hughes, A. E. *Surf. Sci.* **1982**, *121*, 181.

(14) Lamy, C.; Leger, J. M.; Clavilier, J.; Parsons, R. *J. Electroanal. Chem.* **1983**, *150*, 71.

(15) Endo, M.; Matsumoto, T.; Kubota, J.; Domen, K.; Hirose, C. *Surf. Sci. Lett.* **1999**, *441*, L931.

(16) Gland, J. L.; Sexton, B. A.; Fisher, G. B. *Surf. Sci.* **1980**, *95*, 587.

(17) Gland, J. L. *Surf. Sci.* **1980**, *93*, 487.

(18) Matsushima, T. *Surf. Sci.* **1983**, *127*, 403.

(19) Åkerlund, C.; Zoric, I.; Kasemo, B. *J. Chem. Phys.* **1996**, *104*, 7359.

(20) Mieher, W. D.; Ho, W. *Surf. Sci.* **1995**, *322*, 151.

(21) Guo, X.; Winkler, A.; Hagans, P. L.; Yates, J. T., Jr. *Surf. Sci.* **1988**, *203*, 33.

(22) Sawabe, K.; Matsumoto, Y.; Yoshinobu, J.; Kawai, M. *J. Chem. Phys.* **1995**, *103*, 4757.

(23) Ohtani, T.; Kubota, J.; Kondo, J. N.; Hirose, C.; Domen, K. *J. Phys. Chem.* **1999**, *103*, 4562.

(24) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; NSRDS−NBS 39; U. S. Government Printing Office: Washington, DC, 1972; Vol. I.

(25) George, P. M.; Avery, N. R.; Weinberg, W. H.; Tebbe, F. N. *J. Am. Chem. Soc.* **1983**, *105*, 1393.

(26) Avery, N. R. *Appl. Surf. Sci.* **1982**, *11/12*, 774.

(27) Avery, N. R. *Appl. Surf. Sci.* **1982−83**, *14*, 149.

(28) Columbia, M. R.; Thiel, P. A. *Chem. Phys. Lett.* **1994**, *220*, 167.

(29) Ohtani, T.; Kubota, J.; Wada, A.; Kondo, J. N.; Hirose, C.; Domen, K. *Surf. Sci.* **1996**, *368*, 270.

(30) Campuzano, J. C. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1990; Volume 3a, Chapter 4.

(31) Petrie, W. T.; Vohs, J. M. *Surf. Sci.* **1991**, *245*, 315.

(32) Shido, T.; Iwasawa, Y. *J. Catal.* **1993**, *141*, 71.

(33) Pinchas, S.; Laulicht, I. *Infrared Spectra of Labeled Compounds*; Academic Press: London, 1971.

(34) Yamakata, A.; Kubota, J.; Kondo, J. N.; Domen, K.; Hirose, C. *J. Phys. Chem.* **1996**, *100*, 18177.

(35) Ozaki, A. *Isotopic Studies of Heterogeneous Catalysis*; Kodansha Academic Press: Tokyo, 1977.

(36) Yamakata, A.; Kubota, J.; Kondo, J. N.; Hirose, C.; Domen, K.; Wakabayashi, F. *J. Phys. Chem. B* **1997**, *101*, 5177.

(37) Stipe, B. C.; Rezaei, M. A.; Ho, W. *J. Chem. Phys.* **1997**, *107*, 6443.

(38) Jones, A. H.; Poulston, S.; Bennett, R. A.; Bowker, M. *Surf. Sci.* **1997**, *380*, 31.

(39) Davies, P. R.; Mariotti, G. G. *J. Chem. Phys.* **1996**, *100*, 19975.