

Surface matrix isolation method for photoinduced oxidation of carbon monoxide on Pt(111)

Jun Yoshinobu¹, Maki Kawai^{*}

The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan

Abstract

Surface matrix isolation method combined with infrared reflection absorption spectroscopy (IRAS) has been applied to the study of photoinduced oxidation of CO on Pt(111) at 25 K. Multilayer of CO is prepared as a matrix on chemisorbed O₂ and CO molecules, where thermal motions of adsorbed CO and O₂ are frozen. Under D₂ lump irradiation, CO₂ is observed by IRAS as a photochemical product trapped in CO multilayer matrix. This is a strong evidence for our proposed mechanism that the excitation of oxygen atoms is important for the oxidation of CO on Pt(111). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: CO oxidation; Photochemistry; Pt(111); Matrix isolation; IRAS

1. Introduction

Photochemistry of adsorbed molecules on metal surfaces has provided various opportunities for exploring novel surface chemical reactions [1], where adsorbed molecules may desorb from a surface, dissociate or react. Usually the adsorbed states of stable species are studied by surface vibrational spectroscopy [2], and desorbed species are investigated by mass spectroscopy or laser spectroscopy. In this paper, we apply the combination of matrix isolation method [3] and infrared reflection absorption

spectroscopy (IRAS) to the study of surface photochemistry. By the present method, one may detect photodesorbed species or intermediate species in the multilayer matrix together with stable adsorbed species simultaneously.

We have chosen the photoinduced oxidation reaction between adsorbed CO and O₂ on Pt(111) [4,5]. The irradiation induces the dissociation of adsorbed O₂ into oxygen atoms on Pt(111). Before such a nascent oxygen atom accommodates at a stable adsorption site, it may make a collision with adsorbed CO, resulting in the production of CO₂. It has been reported that the CO₂ molecule immediately desorbs from the surface with a certain kinetic energy (~ 0.45 eV) [6]. The desorption dynamics of thus produced CO₂ molecule [6] is quite similar to those in the cases of thermal oxidation of CO on Pt(111) [7–12], suggesting that the transition state of CO₂ desorption is similar. Recently we

^{*} Corresponding author. Tel.: +81-48-467-9405; Fax: +81-462-4663; E-mail: maki@postman.riken.go.jp

¹ Present address: The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan.

have proposed that activated oxygen atoms (nascent, hot, or mobile) play an important role in the production of CO_2 on Pt(111) [13]. In the present experiment this idea is also supported, because thermal motions of adsorbed molecules (CO and O_2) are frozen and energetic O atoms are produced only by the photodissociation on Pt(111) at 25 K.

2. Experimental

The experiments were carried out in an ultra-high vacuum chamber which was equipped with a three-grid retarding field analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy and a quadrupole mass spectrometer for thermal desorption spectroscopy (TDS). The base pressure was $\sim 4 \times 10^{-11}$ Torr. The Pt(111) clean surface was prepared by Ar-ion bombardment, annealing, oxidation and flashing cycles. The sample was cooled down to 25 K by a cryo-refrigerator and was heated up to 1400 K by electron bombardment from the rear. Gaseous O_2 and CO were introduced onto the sample through a pulsed doser and a continuous doser, respectively. Coverages were estimated from TDS and LEED results [13]. A D_2 lamp (Hamamatsu Photonics, L1314) was used as a light source. The broad band (160–400 nm) light irradiated the surface through a fused silica lens and a BaF_2 window with a normal incidence angle. The irradiation intensity at the sample was estimated to be 4 mW cm^{-2} . IRAS spectra were taken with a Fourier transform infrared spectrometer (Mattson RS-1) using an MCT detector, and the resolution was 4 cm^{-1} . The Pt(111) clean surface is served as a background reference for an absorption spectrum.

3. Results and discussion

The $\text{CO} + \text{O}_2/\text{Pt}(111)$ system was prepared by saturating the Pt(111) surface with chemi-

sorbed O_2 at 80 K, followed by adsorption of CO at 25 K. It has been reported that chemisorbed O_2 molecules at saturation form $(3/2 \times 3/2)\text{R}15^\circ$ LEED pattern and the saturation coverage is $\sim 0.44 \text{ ML}$ ($1 \text{ ML} = 1.5 \times 10^{15} \text{ molecules cm}^{-2}$) [14,15]. Based upon electron energy loss spectroscopy [16] and near-edge X-ray absorption fine structure [17] these molecules were identified as a superoxo species with an energy loss peak of 860 cm^{-1} . Recent scanning tunneling microscopy (STM) study reveals that these molecules are imaged as a ‘four-leaf clover’ shape and are centered on bridge sites [18].

Fig. 1 shows a series of IRAS spectra for thermal evolution of the coadsorption system. By adsorption of CO at 25 K, a broad band is observed between 2090 and 2130 cm^{-1} , which is assigned to chemisorbed CO species on the O_2 chemisorbed Pt(111) surface [13]. The very broad band indicates that the adsorbed states are

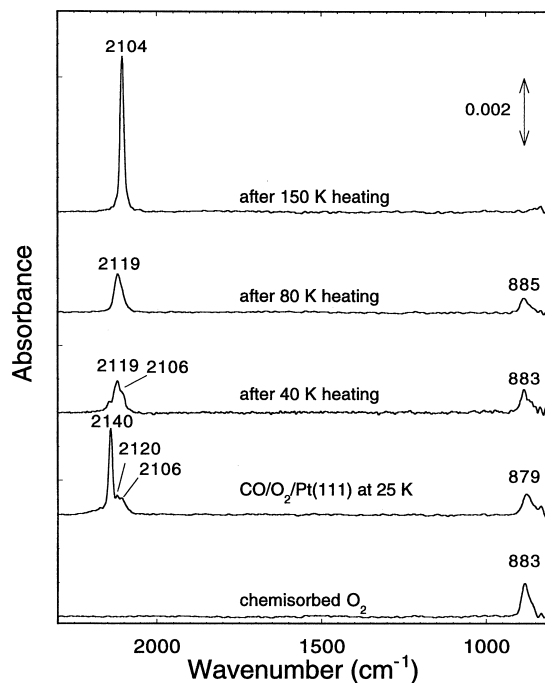


Fig. 1. Thermal evolution of IRAS spectra of the $\text{CO}/\text{O}_2/\text{Pt}(111)$ system. $\theta(\text{O}_2) = 0.44 \text{ ML}$, and $\theta(\text{CO}) = \sim 0.8 \text{ ML}$. $1 \text{ ML} = 1.5 \times 10^{15} \text{ molecules cm}^{-2}$. The sample was heated to an indicated temperature and cooled to 25 K. Spectra were taken at 25 K.

inhomogeneous. The coverage of chemisorbed CO on O₂ preadsorbed Pt(111) was estimated to be 0.2 ML. With increasing the exposure, the band at $\sim 2140\text{ cm}^{-1}$ continuously increases in its intensity, indicating the multilayer formation. A band at 2140 cm^{-1} is ascribed to physisorbed CO molecules, because the wavenumber of this band is close to that of the gaseous CO stretching vibration at 2143 cm^{-1} [19]. Here, the O–O stretching vibration is observed at 879 cm^{-1} .

The surface was heated to an indicated temperature and re-cooled to 25 K, and IRAS measurement was performed. After heating to 40 K, the band at $\sim 2140\text{ cm}^{-1}$ almost disappears as a result of thermal desorption of physisorbed CO molecules around 30 K. With increasing the annealing temperature to 80 K, the band at $\sim 2119\text{ cm}^{-1}$ has increased in intensity and the peak shape became smooth. This is understood by the increase in the dynamic dipole moment due to the rearrangement of chemisorbed CO by the annealing. Even after the annealing the band width is relatively broad ($\sim 25\text{ cm}^{-1}$ full width at half maximum, FWHM), indicating that the adsorbed states of CO with O₂ are inhomogeneous [13].

By heating the surface further, the dissociation of adsorbed O₂, the desorption of O₂ and the CO₂ desorption take place between 100 K and 150 K [10,12,13]. The CO₂ desorption at this temperature range is ascribed to the reaction between nascent oxygen atoms from the O₂ dissociation and adsorbed CO molecules [12,13]. IRAS spectrum after 150 K heating shows a band at 2104 cm^{-1} (8.6 cm^{-1} FWHM), which is assigned to the terminal CO species coadsorbed with disordered oxygen atoms [13]. However, since all CO₂ molecules are desorbed from the surface, no band ascribed to CO₂ is observed by IRAS.

Next, 'the multilayer CO + chemisorbed O₂' on Pt(111) is irradiated by the D₂ lamp at 25 K. During the irradiation, IRAS spectra were continuously recorded (Fig. 2). With the increase of irradiation time, a new band at 2340 cm^{-1} develops. The 2340 cm^{-1} band is ascribed to

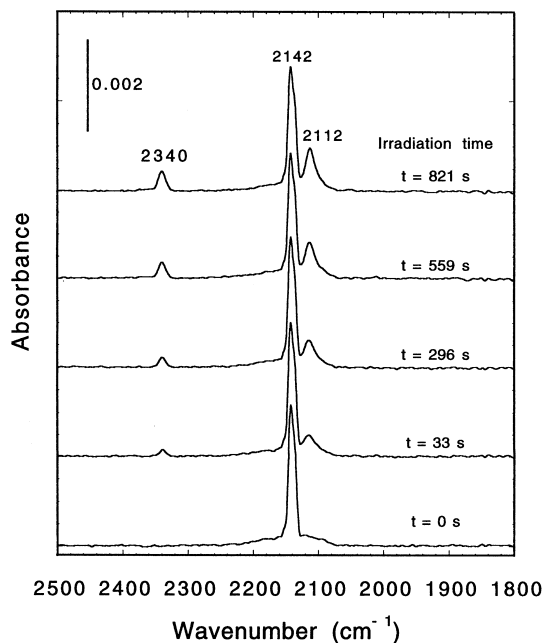


Fig. 2. A series of IRAS spectra of the CO/O₂/Pt(111) system as a function of irradiation time. $\theta(\text{O}_2) = 0.44\text{ ML}$, and $\theta(\text{CO}) = \sim 1\text{ ML}$. A broad band light from a D₂ lamp was used, and the irradiation intensity was 4 mW cm^{-2} . Spectra were taken at 25 K. Total irradiation time is 0, 33, 296, 559 and 821 s from bottom to top spectra.

the CO₂ antisymmetric stretching mode of trapped CO₂ molecules in the CO multilayer matrix, because the wavenumber of this band is close to that of the solid CO₂ at 2344 cm^{-1} [20]. The amount of CO₂, estimated from the integrated absorbance, grew linearly to the irradiation time, indicating that the reaction proceeded as a two-body collision in the time period shown in Fig. 2. Note that without multilayer of CO, the CO₂ formed by photoinduced oxidation of chemisorbed CO should desorb immediately from the surface into vacuum [4–6].

On the other hand, the band of CO multilayer ($\sim 2142\text{ cm}^{-1}$) decreases in its intensity slightly, and a broad band of chemisorbed CO changes to a sharper band at 2112 cm^{-1} with an increased intensity. By the irradiation, the coadsorbed O₂ molecules are dissociated and a part of oxygen atoms are consumed to form CO₂ and the remaining oxygen atoms are adsorbed on the surface. As a result, CO molecules be-

come chemisorbed with oxygen molecules and dissociated atoms on Pt(111), and the band intensity increases as similar to the case of thermal reaction (Fig. 1). Because the CO molecules are coadsorbed with O₂ molecules and O atoms, the ν_{CO} was observed at the frequency between that coadsorbed with O₂ molecules and O atoms.

The present observation has two important points. First, the product CO₂ molecules in the CO matrix are directly observed by means of IRAS. Thus, ‘surface matrix isolation method with IRAS’ may be applicable to detecting photodesorbed species and also intermediate species in the matrix as well as stable adsorbed species simultaneously. Second, the motions of adsorbed molecules (migration, hopping, etc.) are frozen in multilayer matrix at low temperature. Here, thermal motions of adsorbed CO and O₂ are suppressed. Under such condition, certain species may be selectively excited by photoirradiation and others are frozen: oxygen atoms are created from the photodissociation of chemisorbed O₂, and hot (nascent) oxygen atoms thus created attack CO molecules to form CO₂.

This is a strong evidence for our proposed mechanism that the excitation of oxygen atoms is important for the oxidation of CO on Pt(111) [13]. So far it has been generally supposed that a mobile CO would approach a ‘fixed oxygen atom’ to form CO₂ in the thermal oxidation between chemisorbed CO and O on Pt(111) [10,12]. On the other hand, a-CO₂ desorption originates from the reaction between chemisorbed CO and nascent O which is produced by thermal dissociation of chemisorbed O₂ at ~ 120 K [12]. In the photoinduced oxidation between chemisorbed CO and O₂ on Pt(111), it has been originally postulated that photogenerated hot O atoms or excited O₂ molecules are involved [4–6]. However, CO₂ desorption dynamics is quite similar for the thermal oxidation of CO and O, CO and O₂ [11,12] and the photoinduced oxidation between CO and O₂ [6], where the product CO₂ has greater translational and internal energy than that expected from

Boltzmann distributions at surface temperatures, and the angular distribution is oriented towards the surface normal, indicating that the transition state should be similar [11,13].

The key process of the reaction between CO and O₂ is the dissociation of O₂, especially the behavior of recoiled O atoms just after the dissociation. Dissociation of O₂ has been observed by heating the surface to temperatures above 100 K [16], UV light irradiation [4] and electron bombardment [21]. In an STM study, oxygen atoms as thermal dissociation products are found to locate in pairs on Pt(111), occupying fcc sites and the distances between the paired O atoms are within a few lattice constants apart [22]. Dissociation of a single O₂ molecule through a resonant inelastic tunneling using an STM tip is demonstrated on Pt(111) at 50 K [18]. The dissociated O atoms are found to place one to three lattice constants apart, similar to those for the thermal dissociation. Stipe et al. explained that the dissociation is induced by intermolecular vibrational excitation via resonant inelastic tunneling through an adsorbate-induced resonance. In this mechanism, the O₂ bond is assumed to break as soon as its excitation reaches the level that overcomes the dissociation barrier and dissociated O atoms recoil and are trapped at one to three lattice constants apart. Similar dissociation mechanism dominates in the case of photodissociation. Thus, dissociated hot O atoms will site-hop before they are accommodated on the surface. In all three cases, hot (nascent) O atoms produced by the O₂ dissociation have chance to collide with CO molecule before they are accommodated. Finally, these results are consistent with the fact that the formation of CO₂ was not observed by moving a CO molecule to an O atom on Pt(111) at 4 K using a tip of scanning tunneling microscope [23]. Therefore, we conclude that the excitation of oxygen atom is important for the oxidation of CO on Pt(111).

Note added: During the review of this paper, a study with ab initio density functional theory about CO oxidation on Pt(111) was published

[24]. The low energy pathway and transition state for the reaction are identified, where the predominant barrier is the strength of the bond between the O atoms and the surface. Thus, our proposal ‘the excitation of oxygen species as a trigger for CO oxidation on Pt(111)’ [13] seems to be verified.

References

- [1] X.-L. Zhou, X.-Y. Zhu, J.M. White, Surf. Sci. Rep. 13 (1991) 73.
- [2] J.T. Yates, Jr., T.E. Madey (Eds.), Vibrational Spectroscopy of Molecules on Surfaces, Plenum, New York, 1987.
- [3] E. Whittle, D.A. Dows, G.C. Pimentel, J. Chem. Phys. 22 (1954) 1943.
- [4] W.D. Mieher, W. Ho, J. Chem. Phys. 91 (1989) 2755.
- [5] W.D. Mieher, W. Ho, J. Chem. Phys. 99 (1993) 9279.
- [6] V.A. Ukraintsev, I. Harrison, J. Chem. Phys. 96 (1992) 6307.
- [7] T. Engel, G. Ertl, Adv. Catalysis 28 (1979) 1.
- [8] R.L. Palmer, J.N. Smith Jr., J. Chem. Phys. 60 (1974) 1453.
- [9] C.T. Campbell, G. Ertl, H. Huipers, J. Segner, J. Chem. Phys. 73 (1980) 5862.
- [10] T. Matsushima, Surf. Sci. 127 (1983) 403.
- [11] C.B. Mullins, C.T. Rettner, D.J. Auerbach, J. Chem. Phys. 95 (1991) 8649.
- [12] K.H. Allers, H. Pfnuer, P. Feulner, D. Menzel, J. Chem. Phys. 100 (1994) 3985.
- [13] J. Yoshinobu, M. Kawai, J. Chem. Phys. 103 (1995) 3220.
- [14] H. Steininger, S. Lehwald, H. Ibach, Surf. Sci. 123 (1982) 1.
- [15] A. Winkler, X. Guo, H.R. Siddiqui, P.L. Hagans, J.T. Yates Jr., Surf. Sci. 201 (1988) 419.
- [16] N.R. Avey, Chem. Phys. Lett. 96 (1983) 371.
- [17] D.A. Outka et al., Phys. Rev. B 35 (1987) 4119.
- [18] B.C. Stipe, M.A. Rezaei, W. Ho, S. Gao, M. Persson, B.I. Lundqvist, Phys. Rev. Lett. 78 (1997) 4410.
- [19] T. Shimanouchi, Tables of Molecular Vibrational Frequencies, Vol. I, NSRDS-NBS39, 1972.
- [20] W.E. Osberg, D.F. Hornig, J. Chem. Phys. 20 (1952) 1345.
- [21] T.M. Orlando et al., J. Chem. Phys. 93 (1990) 9197.
- [22] J. Wintterlin, R. Schuster, G. Ertl, Phys. Rev. Lett. 77 (1996) 123.
- [23] P. Zeppenfeldt, D. Eiglar, personal communication.
- [24] A. Alavi, P. Hu, T. Deutsch, P.L. Silvestrelli, J. Hutter, Phys. Rev. Lett. 80 (1998) 3650.