Real Time Observaion of Decomposition of Methanol on Ru(001)-p(2X2)-O by a Temperature Programmed ESDIAD/TOF System

Takehiko Sasaki, Yuichiro Itai, and Yasuhiro Iwasawa*
Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received July 16, 1997; CL-970554)

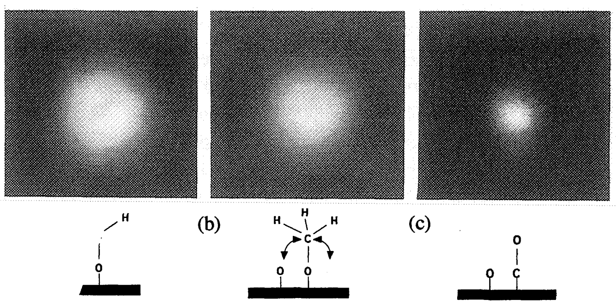
For the purpose of utilizing ESDIAD (Electron Stimulated Desorption Ion Angular Distribution) as a real time probe for surface chemical processes, we have developed a new instrument which can measure ESDIAD images and time of flight (TOF) spectra of desorbed ions in temperature programmed surface processes. TOF measurements are carried out to identify the mass of desorbed ions and to determine their kinetic energy distribution. This temperature-programmed (TP)- ESDIAD/TOF system was used to observe the decomposition processes of methanol on Ru(001)-p(2X2)-O. A halo pattern from the methyl group of methoxy species was observed at 100-200 K by the use of CH$_3$OD, followed by a broad pattern from the methyl group at 230-250 K, and by a near-center pattern from the oxygen atom of CO above 300 K.

ESDIAD has been widely used to investigate the conformation of adsorbates on solid surfaces and to observe change in adlayers by the anneal-quench cycles or during the cooling processes.[1] Instrumentation developments with digital ESDIAD systems were made by Yates and co-workers,[2] while mass-selected ESDIAD images, derived by adopting a pulse-gated detection system, were obtained by Madey and co-workers.[3,4] For the purpose of monitoring surface reactions in real time using ESDIAD, we have developed a TP-ESDIAD/TOF system which can measure ESDIAD images and TOF spectra of desorbing ions during the course of temperature programmed reactions and also at a fixed temperature.[5] It is noted that TOF measurements, which are used for the identification of the mass and the translational energy distribution of the desorbed ions, have been carried out by several groups.[6-14] Ueda et al. developed a TOF-ESD system which can also measure ESDIAD.[8,9] Daimon et al. developed a display type analyzer and have applied it to ESDIAD and TOF measurements.[10-12] Recently Ahner et al. have reported TOF-ESDIAD measurement acquiring a momentum resolved ESDIAD image.[15]

In this study the decomposition processes of methanol on Ru(001)-p(2X2)-O was monitored by the TP-ESDIAD/TOF system. HREELS studies of the decomposition of methanol on clean and oxygen covered Ru(001) have been published by Hrbek et al.[16,17] On Ru(001)-p(2X2)-O adsorption of methanol at 85 K yields methoxy group (CH$_3$-O) and adsorbed hydrogen. Dehydrogenation of methoxy group proceeds upon annealing the sample above 230 K to give adsorbed CO molecules and hydrogen atoms. Not only methoxy species but also adsorbed water are formed in the case of methanol adsorption on clean Ru(001).[16] The aim of this study is to observe methoxy species and its decomposition processes in real time by the newly built TP-ESDIAD/TOF system. Mono-deuterated methanol (CH$_3$OD) was adopted to focus our attention on the change in methoxy species. We have found that ESD yield of deuterium ion (D^+) from D/Ru(001) prepared by the exposure to 10 L D_2 at 100 K is less than the detection limit because of the strong neutralization effect compared to proton. Therefore, if CH$_3$OD is used, adsorbed deuterium would not contribute to the ESDIAD image and only methoxy species could be monitored. It is noted that D^+ was detected for ND$_3$ chemisorbed on Ru(001) with an intensity by a factor of 7 smaller than that for NH$_3$. Takano et al. reported the ESD of D^+ from Ni(110), of which intensity was 6% of that for H^+, after the exposure to 100 L D_2 at 800 K.[18]

Experiments were performed in a UHV chamber equipped with a quadrupole mass spectrometer (QMS), LEED/AES optics and TP-ESDIAD/TOF system.[5] TP-ESDIAD images were acquired during annealing the sample at a rate of 0.5 K/s, commencing from 100 K, using a PID (Proportional Integral Derivative) temperature controller. Temperature-programmed surface processes were observed with ESDIAD in real time by arranging a pulsed incident electron beam for ESDIAD operation which is synchronized out of time phase with a pulsed heating current; by this means it is possible to measure the angular distributions of desorbed ions without distortion of their trajectory by the heating current. TP-ESDIAD images on the phosphor screen behind MCP were recorded by a SIT (Silicon Intensifier Target) camera and stored on video tapes. TP-ESDIAD images were obtained by integrating thirty NTSC video frames corresponding to 1 second followed by digitization. The primary energy for all ESD measurements in the present study was 350 eV. The bias voltage applied to the Ru(001) sample during temperature control and with all ESDIAD measurements was 65 V. An ESDIAD image at 550 K was used to characterize the background due to the emission of soft X-ray stimulated by the incident electron beam. This background image is subtracted from all ESDIAD images which can be displayed as polar angle distributions as a function of temperature. TOF measurements with a bias voltage of 95 V were carried out independently of the ESDIAD measurements. TOF spectra were obtained after 10^5 scans corresponding to the data acquisition time of 1 min with time resolution of 10 ns at a fixed temperature.

Figure 1 shows ESDIAD images taken for Ru(001)-



1. Serial ESDIAD images in temperature programmed reaction of d methanol on Ru(001)-p(2X2)-O. (a) ESDIAD image for methoxy s formed by adsorption of 1.5 L methanol at 100 K. (b) ESDIAD image obtained after the surface was annealed to 230 K. (c) ESDIAD image for CO formed after annealing to 360 K.

p(2X2)-O surface dosed with 1.5 L of CH_3OD at 100 K (a) and the same surface after annealing to 230 K (b) and 360 K (c). This exposure condition gives the saturated chemisorbed layer of methoxy species. A halo pattern in Figure 1a corresponds to the off-normal C-H bonding configuration with random azimuthal orientation. This is the first ESDIAD observation for methoxy species. The halo pattern reveals that the C-O axis of methoxy species is perpendicular to the surface. In the case of methanol adsorption on clean Ru(001) (not shown) halo pattern was not observed, indicating that the configuration of methoxy species was rather disordered on the clean surface. This difference has not been expected from previous studies.[16,17] Guo et al. observed the superposition of normal component from coexisting OH group and off-normal pattern from CH_3 group of acetate species on TiO_2(110) surface.[19] Figure 1b was taken after the surface was annealed to 230 K. The halo pattern was transformed to a broad feature along the surface normal, which indicates that the decomposition intermediates is disordered. Annealing to 360 K yielded a sharp pattern along the surface normal (Figure 1c), which corresponds to the adsorbed CO[20,21] which was formed after dehydrogenation of methoxy species and desorption of hydrogen. In this process the bond inversion occurs from methoxy species which bonds to the surface via O atom to CO with the C-end bonded to the surface, indicating that the large amplitude rocking motion of the methyl group is necessary for the dehydrogenation.

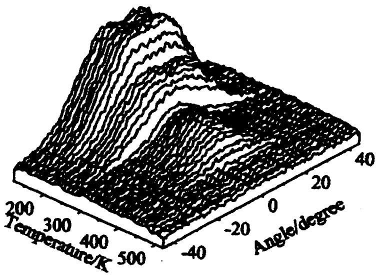


Figure 2. TP-ESDIAD images as a function of temperature measured for Ru(001)-p(2X2)-O dosed with 1.5 L of methanol at 100 K; a heating rate : 0.5 K/s; bias voltage : 65 V.

Figure 2 shows the polar angle distributions of ESDIAD patterns as a function of temperature in the range from 100 K to 500 K obtained by the continuous heating at the rate of 0.5 K/s. The halo pattern of methoxy species remains unchanged up to 200 K, above which the ESDIAD image began weakened and broadened. The sharp pattern above 300 K corresponds to the desorbing O ions from CO. This pattern diminishes at 500 K due to desorption of CO.

In order to identify ionic species contributing to the ESDIAD images TOF measurements were carried out at fixed annealing temperatures. The yield of CO^+ was several times weaker than that of O^+. As described above, D^+ ion was not detected. Figure 3 shows the ESD ion yields of H^+ and O^+ as a function of temperature. Below 200 K H^+ is the only desorbing ion. The decrease of H^+ yield at 180-220 K is associated with the recombinative desorption of methanol from methoxy species and adsorbed hydrogen, as found in TPD spectra. The decrease of H^+ yield between 240 K and 280 K corresponds to the decomposition of methoxy species. Thermal desorption of hydrogen takes place in the temperature range between 250 K and 500 K, which does not affect the profile of H^+ yield. The feature of O^+ yield shows that the onset of CO formation is at 200 K. The yield of O^+ continues to increase up to 360 K, at which most of hydrogen has desorbed thermally. This behavior is attributed to the site change of CO due to the competition with adsorbed hydrogen because the yield of O^+ from CO is dependent on the site occupation.[5] At 540 K O^+ signal still remains at nonzero value. The strong feature along the surface normal was weakened up to 500 K and only a weak broad feature was left. This component might be related to either predosed oxygen or the tailing on the high temperature side of the CO TPD peak. In cases of pure CO adsorption and pure methanol adsorption O^+ yield reaches zero at 500 K.

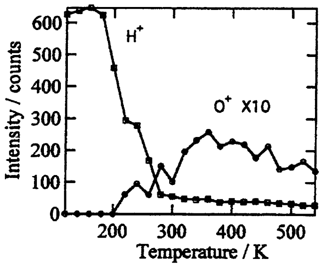


Figure 3. ESD intensities of H^+ and O^+ as a function of temperature obtained by TOF measurements for Ru(001)-p(2X2)-O dosed with 1.5 L of methanol at 100 K. Square: H^+. Circle: O^+ magnified by a factor of 10.

In summary methoxy species and its decomposition processes were investigated in real time by the TP-ESDIAD/TOF system. Perpendicular alignment of methoxy species on Ru(001)-p(2X2)-O surface was observed. This study illustrates the role of TP-ESDIAD/TOF system together with other conventional surface science techniques in providing insight of adsorption and reaction processes at surfaces.

This work has been supported by CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Corporation (JST).

References

1 R. D. Ramsier and J. T. Yates Jr., *Surf. Sci. Rep.*, **12**, 243 (1991).
2 M.J.Dresser, M.D.Alvey, and J.T.Yates Jr., *Surf. Sci.*, **169**, 91 (1986).
3 S. A. Joyce, A. L. Johnson, and T. E. Madey, *J. Vac. Sci. Technol. A*, **7**, 2221 (1989).
4 N. J. Sack, L. Nair, and T. E. Madey, *Surf. Sci.*, **310**, 63 (1994).
5 T. Sasaki and Y. Iwasawa, *Surf. Sci. Lett.*, in press.
6 R.Stockbauer, E.Bertel, and T.E.Madey, *J.Chem.Phys.*, **76**, 5639 (1982).
7 N. D. Shinn and T. E. Madey, *Surf. Sci.*, **180**, 615 (1987).
8 K. Ueda and A. Takano, *Jpn. J. Appl. Phys.*, **27**, L2029 (1988).
9 K. Ueda and A. Takano, *Jpn. J. Appl. Phys.*, **28**, 2594 (1989).
10 H. Daimon, *Rev. Sci. Instrum.*, **59**, 545 (1988).
11 H. Daimon and S. Ino, *Vacuum*, **41**, 215 (1990).
12 K. Sakamoto, K. Nakatsuji, H. Daimon, T. Yonezawa, and S. Suga, *Surf. Sci.*, **306**, 93 (1994).
13 I. Arakawa, M. Takahashi, and K. Takeuchi, *J. Vac. Sci. Technol. A*, **7**, 2090 (1989).
14 S. L. Bennett, C. L. Greenwood, and E. M. Williams, *Surf. Sci.*, **290**, 267 (1993).
15 J. Ahner, D. Mocuta, R.D. Ramsier, and J.T. Yates,Jr. *J. Vac. Sci. Technol. A*, **15**, 1548 (1997).
16 J.Hrbek, R.A.de Paola, and F.M. Hoffmann, *J.Chem.Phys.*, **81**, 2818 (1984).
17 J.Hrbek, R.A.de Paola, and F.M.Hoffmann, *Surf.Sci.*, **166**, 361 (1986).
18 A.Takano and K. Ueda, *Jpn. J. Appl. Phys.*, **32**, 1217 (1993).
19 Q.Guo, I.Cocks, and E.M.Williams, *J.Chem. Phys.*, **106**, 2924 (1997).
20 T.E. Madey, *Surf. Sci.*, **79**, 575 (1979).
21 P.Feulner, R.Treichler, and D. Menzel, *Phys. Rev. B*, **24**, 7427 (1981).