Thermal and photo-induced oxidation of CH_2 on Cu(100)

Imre Kovács [1], Frigyes Solymosi [*]

Institute of Solid State and Radiochemistry, A. József University and Reaction Kinetics Research Group of the Hungarian Academy of Sciences [2], P.O. Box 168, H-6701 Szeged, Hungary

Abstract

The oxidation of the CH_2 species produced by thermal and photo-induced dissociation of CH_2I_2 has been followed by X-ray and ultraviolet photoelectron spectroscopies and temperature programmed spectroscopy. Preadsorbed oxygen atoms hindered the thermal dissociation of CH_2I_2. The dominant pathway of CH_2 formed above 200 K is its coupling into C_2H_4, which interacted with adsorbed O atoms. Formaldehyde formation was not observed. However, CH_2 produced by illumination of adsorbed CH_2I_2 at $\sim$ 100 K combined with adsorbed O to give CH_2O. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic synthesis of oxygenated hydrocarbon compounds is an important project for heterogeneous catalysis [1]. In order to develop an efficient catalyst and to elaborate the mechanism of the catalytic reactions, we have to know more about the elementary steps of the oxidation processes. The study of the oxygen addition to hydrocarbon fragments (CH_2, CH_3 and C_2H_5) on catalyst surfaces is strongly related to this project. Our first attempt to produce methoxy species in the reaction of adsorbed CH_3 and O atom on Pd/SiO_2 catalyst was not successful, very likely due to large inactive area of the support [2]. Positive results were obtained, however, on metal single crystal surfaces under UHV conditions. It was found that CH_2 reacts with adsorbed O atoms to give CH_2O above 170–200 K on Pt(111) [3], Rh(111) [4–8] and Pd(100) [9]. In the study of the oxidation of CH_3, methoxy was identified on Pd(100) [9] and Rh(111) [10–12], which oxidized further to CO_2 and H_2O at higher temperature. The oxidation of C_2H_5 species on Rh(111) produced acetaldehyde (T_p = 340 K) very likely through the formation of ethoxy species [10,13].

In the present work, we examine the interaction of CH_2 with adsorbed O atoms on Cu(100) surface. The reactivity of Cu is basically different from that of Pt metals, as CH_2, instead of decomposition and self-hydrogenation, is coupled readily into ethylene, which desorbs at higher temperatures [14–16].

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[*] Corresponding author. Fax: +36-62-322378

[1] Present address: Department of Surface Chemistry and Catalysis, Institute of Isotopes, P.O. Box 77, Budapest, Hungary.

[2] This laboratory is a part of the Center for Catalysis, Surface and Material Science at the József Attila University of Szeged.

2. Experimental

The experiments were performed in standard ultrahigh vacuum system, with a background pressure of 5×10^{-10} mbar, equipped with facilities for Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and temperature programmed spectroscopy (TPD) [9,10]. Preparation and cleaning of the Cu(100) crystal have been described previously [17]. The UV light source was a focused 30 W Hg lamp. The light passed through a high purity sapphire window into the vacuum chamber. The incident angle was 30° off the normal surface.

3. Results and discussion

3.1. Dark experiments

From previous XPS and TPD studies, it was concluded that the adsorption of CH_2I_2 on a clean Cu(100) surface is dissociative at submonolayer coverages (< 0.3 ML, ML = monolayer) at 90 K, but molecular at higher coverages. The dissociation of adsorbed monolayer started above 173 K and completed at 205 K [16]. XPS measurements show that the uptake of CH_2I_2 on oxygen-dosed Cu(100), $\theta_O = 0.5$, at different CH_2I_2 exposures is practically the same as for the clean surface. At and above monolayer, the position of the binding energy of $I(3d_{5/2})$ appeared at 620.75 eV, which corresponds to the molecularly adsorbed CH_2I_2. A broading of the I peak, indicating the onset of the dissociation of CH_2I_2, occurred at higher temperature, 210 K, compared to the clean surface (Fig. 1A). A final value of the I(3d) peak, 619.75 eV, indicating the completeness of the dissociation, is attained at 268 K. Accordingly,
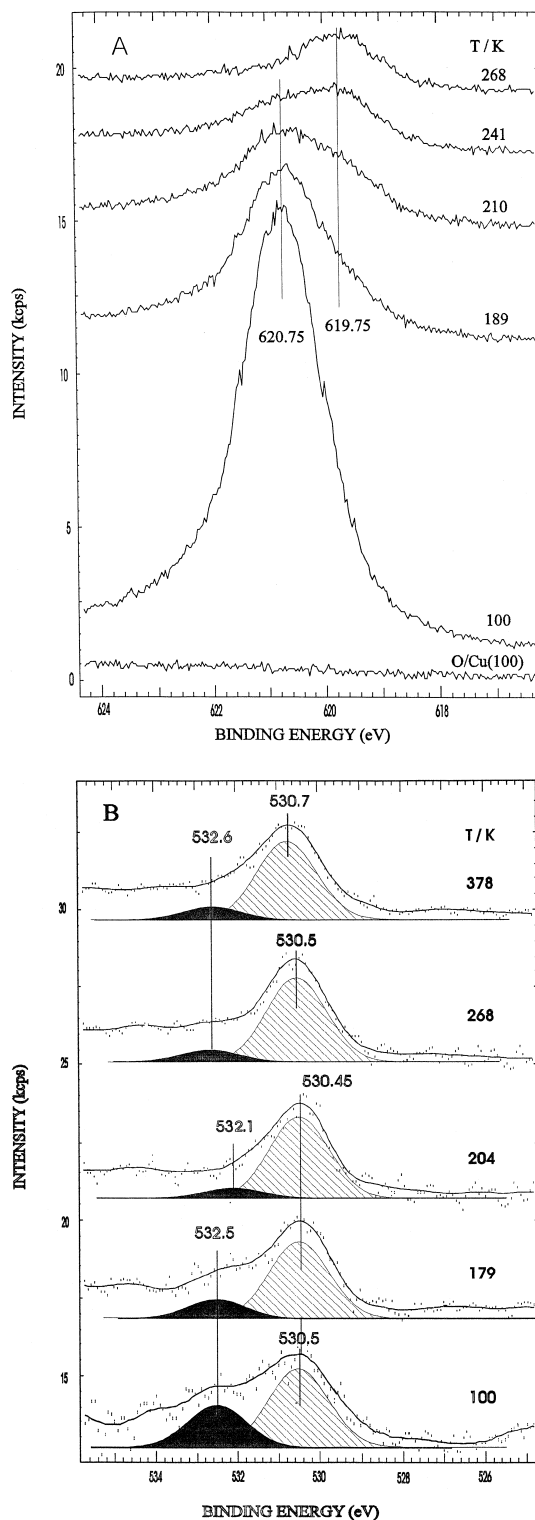

Fig. 1. Effects of annealing on the position of the (A) $I(3d_{5/2})$ and (B) O(1s) binding energies in the XPS spectra of adsorbed CH_2I_2 on oxygen-dosed Cu(100).

the preadsorbed oxygen even at saturation coverage, which corresponds to $\theta_O = 0.5$, could not alter the uptake of CH_2I_2. However, it shifted the temperature of the complete dissociation of CH_2I_2 to higher temperature, by about 60 K. This is very likely due to the occupation of some adsorption sites. Similar features were found on Rh(111) and Pd(100) surfaces [5,6,9]. The C(1s) signal was observed at 284.4 eV at 100 K. It underwent a marked attenuation around 200 K, and shifted to 283.8 eV above 240–260 K.

A significant change occurred in the O(1s) region. Whereas the adsorbed oxygen on a clean Cu(100) gave a single peak at 530.2 eV, exposing this O-covered Cu to CH_2I_2 caused the appearance of a new peak centered at 532.5 eV. Annealing the adsorbed layer led to the attenuation of this new O(1s) peak and a shift to lower binding energy, 532.2 eV at 179 K, 531.7 eV at and above 204 K. This peak can be traced up to 378 K. The main O peak at 530.5 eV changed

very little up to 700 K. Some selected XP spectra are presented in Fig. 1B. This spectral feature may indicate an interaction of adsorbed O atoms with methylene iodide in the adsorbed layer and/or the formation of a new surface species.

The reaction in the coadsorbed layer was followed by TPD measurements. In the case of a clean surface CH_2I_2 desorbed only in one peak (α) with $T_p = 210$ K, which was attributed to the desorption of a multilayer [14–16]. In the presence of preadsorbed O, the temperature of this peak shifted to lower temperature, $T_p = 198$ K (at $\theta_O = 0.2$), and a new peak (β) developed with $T_p = 225$ K. Further increase in the oxygen coverage to $\theta_O = 0.5$ somewhat decreased the amount of CH_2I_2 desorbed in the α peak, and enhanced that desorbing in the β peak. (Fig. 2A). In Fig. 2B, we present the effect of CH_2I_2 exposure on its desorption at $\theta_O = 0.5$. A clear increase in the β peak is experienced with the rise of the exposure.
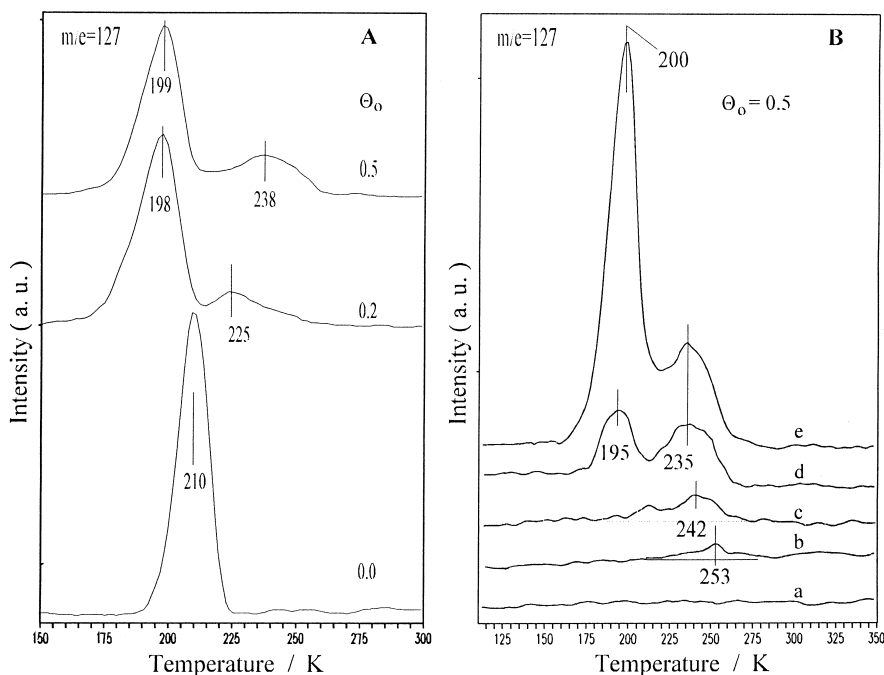

Fig. 2. (A) Effects of oxygen coverage on the TPD spectra of CH_2I_2. Exposure of CH_2I_2 was 0.33 L. (B) Desorption of CH_2I_2 as a function of exposure from oxygen-dosed Cu(100) at $\theta_O = 0.5$.

The product of the reaction of CH_2 formed in the dissociation of CH_2I_2 on a clean Cu(110) was exclusively ethylene [14–16]. Its peak temperature was found to be 240 K by two independent studies [14,16]. A small shoulder at the high temperature side was also observed [16]. In the presence of preadsorbed oxygen, we obtained a dramatic change in the product distribution. The amount of ethylene markedly decreased with the increase of oxygen coverage, and above $\theta_O = 0.12$, no or very little ethylene is formed (Fig. 3). At the same time, H_2O ($T_p = 344$ and 460 K) and CO_2 ($T_p = 550$ and 602 K) are produced. The high peak temperatures suggest that the evolution of both compounds is reaction limited process. A great effort was made to identify CH_2O, H_2, CO, CH_4 and other C_xH_y compounds in the desorbing products without any positive results.

In order to characterize the coadsorbed layer, UPS measurements were performed. Following the adsorption of CH_2I_2 on O-dosed Cu(100)

($\theta_O = 0.5$) at 100 K, photoemission signals appeared at 3.1, 6.9 (7.6), 9.4 and 13.4 eV. Almost the same photoemission lines were obtained for a clean surface, which are characteristic for the molecularly adsorbed CH_2I_2 (Fig. 4). These peaks are assigned to the ($2b_1$, $2b_2$, $1a_2$, $4a_1$), ($2b_1$, $3a_1$) $1b_1$ and $2a_1$ orbitals of adsorbed CH_2I_2 [9,16]. No significant spectral changes occurred up to the temperature of the desorption of weakly adsorbed CH_2I_2. As a result of the desorption, the intensities of the photoemission signals are greatly reduced. At 222 K, when the desorption was complete and the dissociation of CH_2I_2 set in, photoemission signals are seen at 15.7, 13.7, 12.1, 10.8, 9.4, 7.9, 6.8 and 6.2 eV. Heating the coadsorbed layer to 252 K, which completed the dissociation, signals are detected at 15.7, 13.5, 11.2, 9.8, 8.1 and 6.2 eV.

For the facilitation of the identification of adsorbed complexes produced during annealing, in Table 1, we list the photoemission lines of all surface compounds possibly formed in the coad-
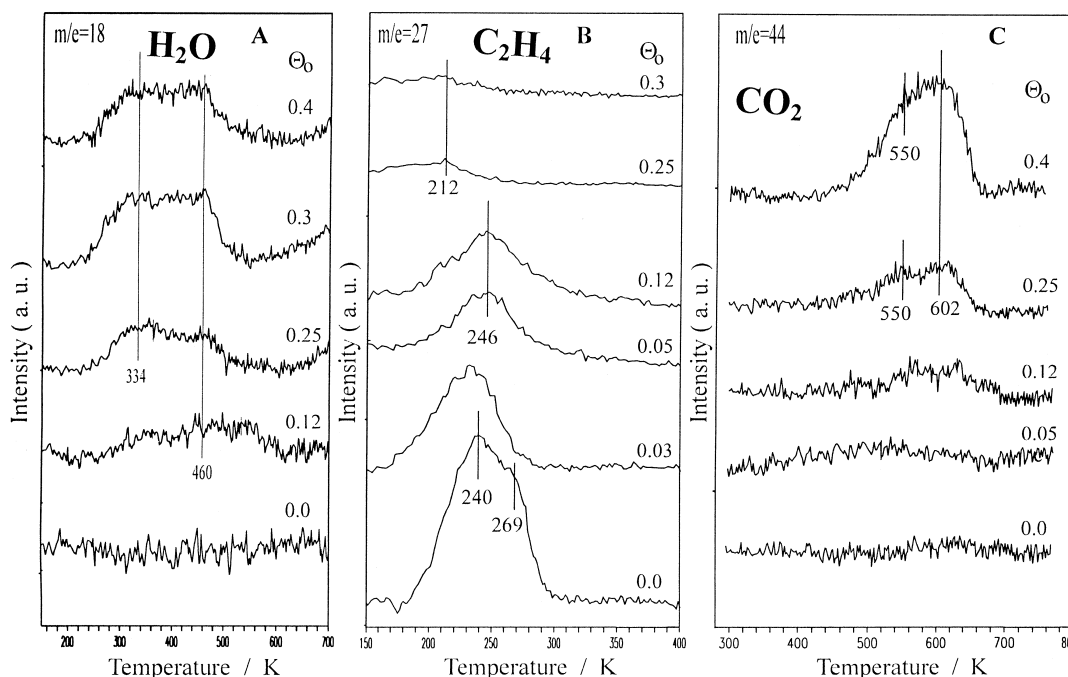

Fig. 3. TPD profiles of various products formed in the oxidation of CH_2 on the oxygen-dosed Cu(100) at different oxygen coverages.
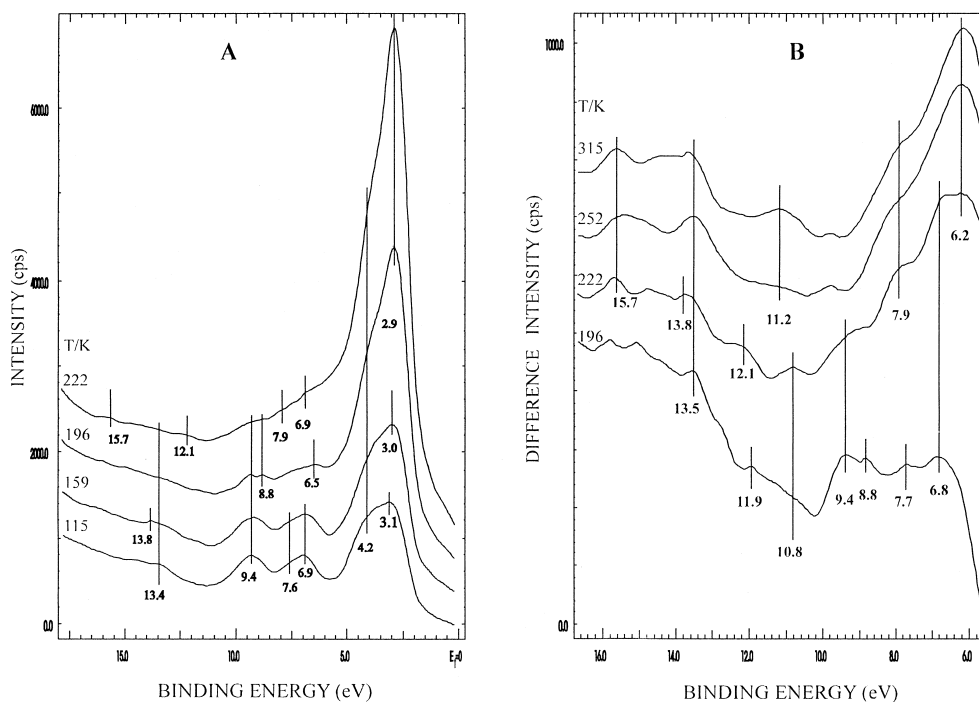
Fig. 4. Effects of annealing on the UPS spectra of adsorbed CH_2I_2 on oxygen-dosed Cu(100). Exposure of CH_2I_2 was 2.0 L at $\theta_O = 0.5$.

sorbed layer. On the basis of this, we may conclude that there is no sign of the existence of adsorbed CH_2, which has a characteristic photoemission line 5.8–6.2 eV [9]. This indicates that the CH_2 formed reacts immediately further. Note that this characteristic is in contrast with the CH_2I_2–Pd(100) and CH_2I_2–Cu(100) systems when the presence of CH_2 was established between 90–213 K [9,16].

On the analogy of CH_2 + O/Rh and CH_2 + O/Pd systems [4–9], we may speculate that CH_2 is coupled with O atoms to give CH_2O

$$CH_2(a) + O(a) = CH_2O(a)$$
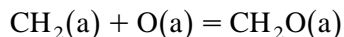
Table 1
Photoemission signals of various adsorbed species

Adsorbed species	Surface	UPS bands (eV)	References
O_{ads}	Cu(poly)	5.5	[18]
	Rh(111)	5.5–5.8	[19]
OH_{ads}	Rh(111)	5.7–6.0	[19]
I_{ads}	Pd(100)	5.8	[20]
$CH_{2,ads}$	Pd(100)	5.9–6.2	[20]
	Cu(100)	5.8	[16]
	Co(poly), Ni(poly)	5.5–5.8	[21]
CH_2I_2	Pd(100)	4.7–5.0, 6.0–6.5, 8.0–8.2, 9.2–9.5, 12.9–13.0	[20]
	Cu(100)	3.8–4.0, 6.7–6.8, 7.4, 9.1–9.3, 13.2	[16]
C_2H_4	Cu(poly)	5.2–5.3, 6.8, 8.3–8.5, 9.7	[18]
C_2H_2	Cu(poly)	5.4, 8.6, 11.0	[18]
CH_2O	Cu(110)	5.6, 9.2, 11.8	[22]
HCOO	Cu(110)	5.4, 8.0, 9.6, 13.0	[22]
	O/Pd(100)	4.9, 7.8, 10.4, 13.2	[23]
	O/Rh(111)	5.3, 8.6, 10.2, 13.2	[19]

which instead of desorption is further oxidized to formate

$$CH_2O(a) + 2O(a) = HCOO(a) + OH(a)$$
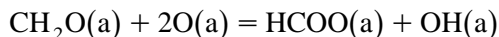
This reaction was observed following the adsorption of CH_2O on oxygen-dosed Cu surface [22]. The UPS spectrum registered after annealing to 252 K, however, corresponds neither to CH_2O nor to HCOO. Note that there was also no sign in XPS of O(1s) for the existence of O-containing adsorbed complexes, such as CH_2O or HCOO. We may also assume the presence of a mixed layer. However, the TPD spectrum obtained is basically different from those taken after oxidation of CH_2O to formate, or after adsorption of HCOOH on O-dosed Cu [22,24]: the products were H_2 and CO_2, which desorbed with the same peak temperature of 475 K. In the present case, we found H_2O desorption (T_p = 344 and 460 K) and CO_2 (T_p = 550 and 602 K). Taking into account all these information and considerations, we tend to exclude the formation of CH_2O in the coadsorbed layer on Cu(100) surface.

Accordingly, the reaction pathway of CH_2 on O-dosed Cu(100) is basically different from that established for Rh and Pd surfaces. It appears that the thermodynamic driving force for the coupling of CH_2 formed above 200 K, is still greater than that for the combination of CH_2 with adsorbed O atoms. The UPS signals observed at 196 and 222 K support this conclusion. However, no desorption of C_2H_4 was measured above $\theta_O \sim 0.12$, therefore, we have to assume that the ethylene formed interacted strongly with adsorbed O atoms to give other adsorbed species.

An interaction of C_2H_4 with adsorbed O on Cu(111) was observed before by Au and Roberts [25,26] and Roberts [27]. They found a development of a strong O(1s) component in the XPS with a binding energy of 531.5 eV at 373 K, which we also detected at and above 204 K (Fig. 1B). This peak was attributed to the forma-
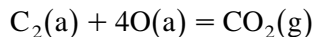
tion of OH-like species. They assumed the occurrence of the reaction

$$C_2H_4 + O(a) = C_2H_3(a) + OH(a)$$
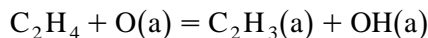
They also stated that the C_2H_3 bonded to adsorbed O atoms, Cu–O–C_2H_3, is stable up to 370 K [25]. Unfortunately, the further reactions of 'C_2H_3' intermediate were not explored, but the formation of C_2H_2 seems very likely. On the basis of the data collected in Table 1, we may suppose that above 222 K, we can count with the existence of adsorbed C_2H_2 and for C_2H_3 species, in addition to adsorbed OH, O and I. The fact that the evolution of CO_2 ($T_p \approx$ 602 K) occurs at much higher temperatures than that of H_2O suggests that first the oxidative dehydrogenation of C_2H_2 proceeds
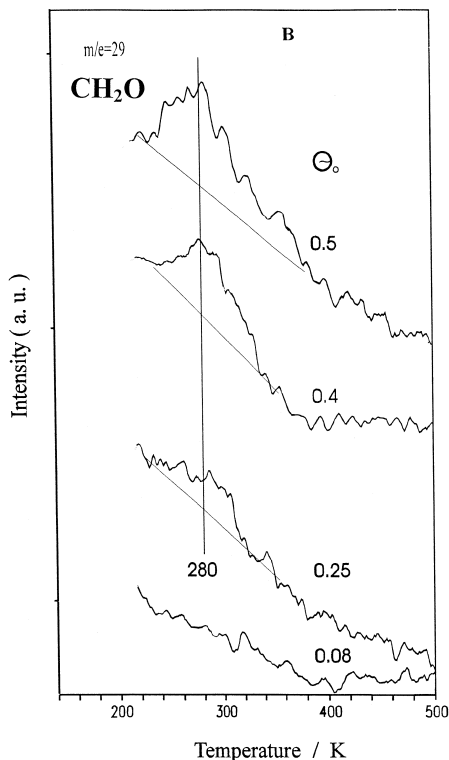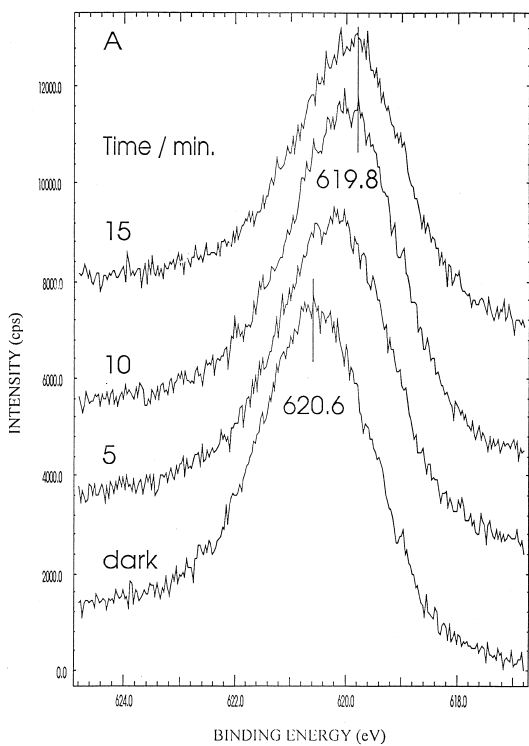
$$C_2H_2(a) + 2O(a) = C_2(a) + 2OH$$

$$C_2H_3(a) + 3O(a) = C_2(a) + 3OH$$

$$2OH(a) = H_2O(g) + O(a)$$
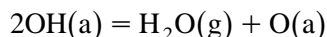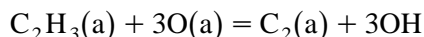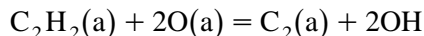
followed by the oxidation of surface carbon

$$C_2(a) + 4O(a) = CO_2(g)$$

This reaction pathway is supported by the observations that adsorbing a small amount of C_2H_4 on O-dosed Cu(100), evolution of H_2O and CO_2 was found practically in the same temperature range as in the present case [23].

3.2. Effects of irradiation

Previous studies on Pd(100) and Rh(111) revealed that irradiation of adsorbed CH_2I_2 at 100 K dramatically enhanced its dissociation and produced adsorbed CH_2 species in large quantity even at such a low temperature [5,6,9]. Some measurements on the effects of irradiation have been performed in the present case, too. XPS studies showed that illumination of coadsorbed layer at 100 K for 15 min caused a shift in the binding energy of $I(3d_{5/2})$ from 620.6 eV to 619.8 eV (Fig. 5), which was a clear indica-

tion of the occurrence to the photo-induced dissociation of adsorbed CH_2I_2 [5,6,9]. As a result of this process, CH_2O formed ($T_p = 280$ K), as revealed by post-irradiation TPD. Its amount increased with the rise of O coverage. At the same time, the peak temperature of CO_2 shifted to lower temperature, 468 K, which agrees well with the T_p values for CO_2 evolution from $CH_2O + O/Cu(111)$ and $HCOO + O/Cu(111)$ systems [28].

In the interpretation of these new features, we point out the significant difference between dark and photo experiments. In the latter case, CH_2 species is produced already at 100 K, whereas in dark experiment this occurs only above 200 K. Accordingly, the coupling of CH_2 at 100 K is restricted, and at low temperatures CH_2 species is combined with O atoms to give CH_2O. A fraction of CH_2O desorbs above 200 K, another fraction is oxidized to formate, which releases H_2 and CO_2 at 468 K.

4. Conclusions

(i) Preadsorbed oxygen atoms did not influence the uptake of CH_2I_2 on Cu(100) at 90 K, but (ii) it shifted the temperature of C–I bond cleavage by about 60 K to higher temperature. (iii) The reaction pathway of the oxidation differs from that established for Rh and Pd surfaces as formaldehyde formation was not observed. (iv) It appeared that the coupling of CH_2 is the dominant pathway on oxygen dosed surfaces, too, and the ethylene formed interacted with adsorbed oxygen atoms. The C_xH_y species formed is oxidized to H_2O and CO_2 above 300 K. (v) Illumination of coadsorbed layer induced the formation of CH_2 even at ~ 100 K which combined with adsorbed O atom to give CH_2O.

Fig. 5. Effects of illumination on the (A) XPS spectra of $CH_2I_2 + O$ coadsorbed system on Cu(100) and (B) on the formation of CH_2O at different oxygen coverages.

Acknowledgements

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