

Adsorption and reactions of CH_2I_2 on Ru(001) surface

A. Kis^a, K.C. Smith^b, J. Kiss^a, F. Solymosi^{a,*}

^a Institute of Solid State and Radiochemistry,

A. József University and Reaction Kinetics Research Group of the Hungarian Academy of Sciences, P.O. Box 168, H-6701 Szeged, Hungary

^b Department of Chemistry and Biochemistry, University of Texas, Austin, TX 78712, USA

Received 1 November 1999; accepted for publication 13 April 2000

Abstract

spectroscopy (UPS), temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and work function measurements. Adsorption of CH_2I_2 is characterized by a work function decrease (0.96 eV at monolayer), indicating that adsorbed CH_2I_2 has a positive outward dipole moment. Three adsorption states were distinguished: a multilayer ($T_p = 200$ K), a weakly bonded state ($T_p = 220$ K) and an irreversibly adsorbed state. A new feature is the formation of CH_3I , which desorbs with $T_p = 160$ K. The adsorption of CH_2I_2 at 110 K is dissociative at submonolayer, but molecular at higher coverages. Dissociation of the monolayer to CH_2 and I proceeded at 198–230 K, as indicated by a shift in the $\text{I}(3d_{5/2})$ binding energy from 620.6 eV to 619.9 eV. A fraction of adsorbed CH_2 is self-hydrogenated into CH_4 ($T_p = 220$ K), and another one is coupled to di- σ -bonded ethylene, which — instead of desorption — is converted to ethylidyne at 220–300 K. Illumination of the adsorbed CH_2I_2 initiated the dissociation of CH_2I_2 monolayer even at 110 K, and affected the reaction pathways of CH_2 . © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alkanes; Alkynes; Ruthenium; Single crystal surfaces; Surface photochemistry; Thermal desorption spectroscopy; X-ray photoelectron spectroscopy

1. Introduction

In the last decade considerable progress has been made in establishing the chemistry of different hydrocarbon fragments (CH_2 , CH_3 , C_2H_5 , C_2H_7 , etc.) on metal single crystal surfaces [1–6]. By means of several surface science tools our knowledge of the bonding, stability and reaction pathways of these hydrocarbon species has been significantly broadened. As C_xH_y fragments are

the possible reaction intermediates in most of the catalytic syntheses involving hydrocarbons, the results obtained may help to refine the mechanisms of these catalytic processes and to develop more efficient catalysts.

In this project an important step was the development of methods for the preparation of C_xH_y species of a given composition. Halogenated hydrocarbons were thought to be suitable sources for these species. The first studies, however, revealed that chloro compounds (CH_2Cl_2 , CH_3Cl , etc.) are quite stable on metal surfaces and dissociate to CH_x and Cl only at high temper-

* Corresponding author. Fax: +36-62-322-378.

E-mail address: fsolym@chem.u-szeged.hu (F. Solymosi)

atures, when CH_x undergoes secondary reactions [7–12]. Iodo compounds were found to be more reactive substances as they dissociate at much lower temperatures [1–6,13,14]. An important further step was the pyrolysis of azomethane to produce CH_3 [15,16].

In the present work we examine the adsorption and dissociation of CH_2I_2 on a Ru(001) surface with the aim of obtaining information on the chemistry of the CH_2 fragment on this surface. Previous studies revealed that the nature of the metal plays a decisive role in both the adsorption and the reaction pathway of the CH_2 formed [17–29]. The chemistry of CH_2I_2 on Ru surfaces has not been investigated yet, but some measurements on the adsorption of the other CH_2 precursor compounds (ketene and diazomethane) were performed [30,31].

2. Experimental

2.1. Methods

The experiments were performed in standard ultrahigh vacuum systems with a background pressure of 5×10^{-10} mbar produced by turbomolecular, ion-getter and titanium sublimation pumps. The chamber was equipped with an electrostatic hemispherical analyzer (Leybold-Hereaus LHS-10), a differentially pumped UV photon (HeI, II) source for ultraviolet photoelectron spectroscopy (UPS), an X-ray source with Al anode for X-ray photoelectron spectroscopy (XPS) and an electron gun for Auger electron spectroscopy (AES) measurements. The angles of the UV source and electron analyzer with respect to the surface normal were 70 and 16°, respectively. All binding energies are referred to the Fermi level. Collection times for UPS and XPS were 15 and 30 min, respectively. XP spectra were smoothed by a fast Fourier transform method. For temperature programmed desorption (TPD), the sample was heated at 10 K/s from 110 K to a selected temperature. The mass spectrometer was in line of sight. Changes in work function were obtained by measuring the secondary electron cut-off in the HeI UP spectra with the sample at -9 V relative to earth.

The UV light source was a focused full arc 40 W Hg lamp. The maximum photon energy at the sample was not greater than 5.4 eV (the onset of UV intensity from the Hg arc lamp). The light passed through a high-purity sapphire window into the vacuum chamber. The incident angle was 30° from the surface normal.

2.2. Materials

The oriented disk-shaped Ru crystal (purity 99.99%, diameter 8 mm, thickness 1.5 mm) was oriented within 0.5° at the (001) face and mechanically polished with diamond paste. The crystal was spotwelded to two 0.25 mm diameter wires for resistive heating and cooled to 110 K by heat conduction to a liquid nitrogen reservoir. The sample was heated from the rear by radiation from a tungsten filament and resistively with the spotwelded Ta wires. The temperature was measured with a chromel–alumel thermocouple junction, fastened to the side of the crystal. Rigorous sample cleaning was done by Ar^+ bombardment to remove oxides and common impurities. Routine cleaning of the surface was accomplished by cycling the crystal temperature between 900 and 1450 K in an O_2 pressure of 1×10^{-8} mbar, as measured by the system's ion gauge. This was followed by annealing at 1550 K to remove adsorbed oxygen. CH_2I_2 was obtained from Fluka and degassed by freeze–pump–thaw cycles prior to use.

3. Results

3.1. Adsorption of CH_2I_2

Fig. 1 shows the XP spectrum of Ru(001) in the iodine region as a function of CH_2I_2 exposure at 110 K. At low exposures, up to 0.6 L, the binding energy of $\text{I}(3d_{5/2})$ was 619.9 eV, which shifted to higher values, up to 620.6 eV, at high CH_2I_2 exposures. The area of the XPS signal for $\text{I}(3d_{5/2})$ is plotted against exposure in Fig. 2A. It increased continuously as a function of CH_2I_2 exposure at 110 K; saturation was not attained.

The interaction of CH_2I_2 with the Ru surface

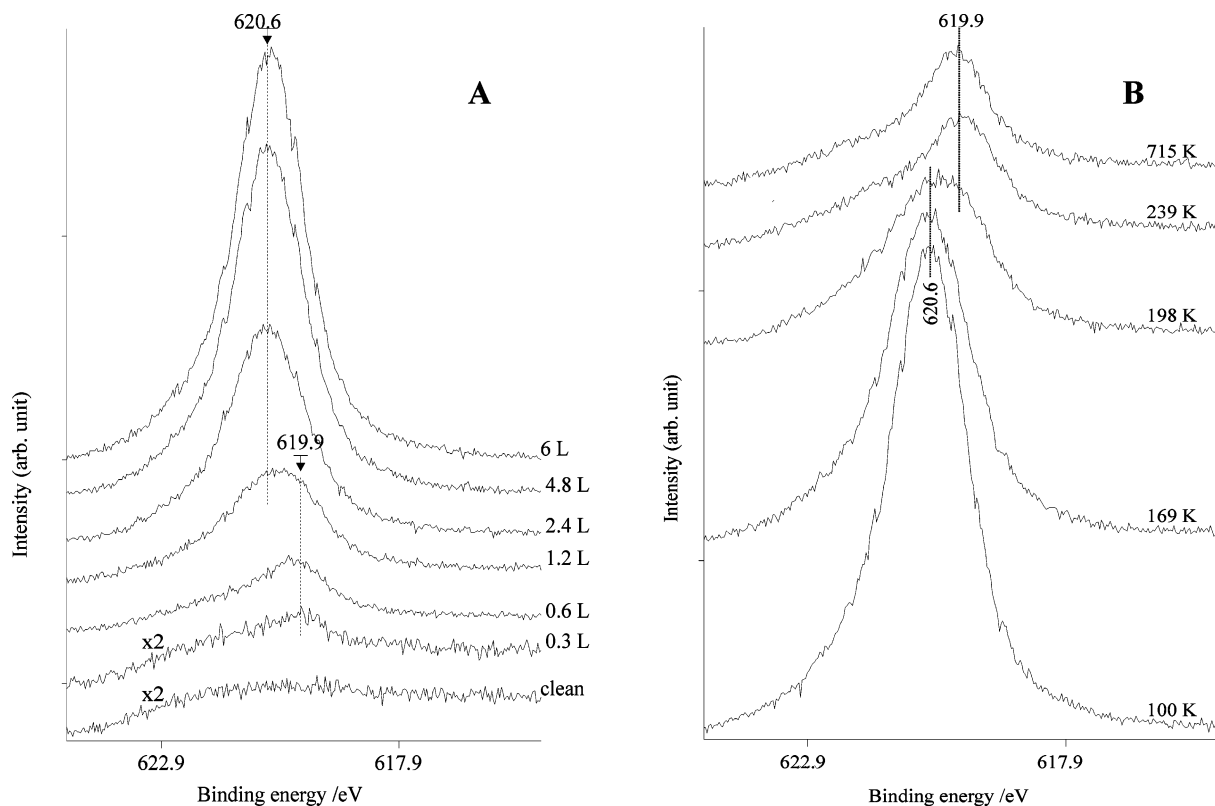


Fig. 1. (A) XP spectra of Ru(001) as a function of CH_2I_2 adsorption at 110 K and (B) after heating the adsorbed layer to different temperatures. CH_2I_2 exposure for (B) was 6 L.

was also followed by work function measurements. The adsorption of CH_2I_2 caused a gradual decrease in the work function of Ru(001), as illustrated in Fig. 2B. The maximum decrease, $\Delta\phi = -0.96$ eV, was attained at an exposure of only 3.0 L.

HeI photoelectron spectra of Ru(001) under the same experimental conditions are displayed in Fig. 3. At a very low exposure (~ 0.3 L) we obtained only one signal at 5.4–5.7 eV. At higher exposure the positions of the photoemission signals were 4.4, 7.3 and 9.7 eV (Fig. 3A). A summary of observed binding energies of adsorbates is given in Table 1.

Thermal desorption curves following CH_2I_2 adsorption on the Ru(001) surface are depicted in Fig. 4. No desorption of CH_2I_2 was seen below an exposure of 1.0–1.5 L. At and above this exposure, a CH_2I_2 peak appeared with $T_p = 220$ K. This peak

is denoted β . On increasing the CH_2I_2 exposure, the amount of desorbed CH_2I_2 increased and finally saturated at 6.0 L of exposure. We assume that the saturation of a monolayer occurred at this exposure. At the same time a new peak developed with $T_p = 200$ K (denoted α) which could not be saturated.

3.2. Effects of annealing of adsorbed layer

XP spectra of adsorbed layers annealed to different temperatures are displayed in Fig. 1B. No shift in the binding energy (BE) of $\text{I}(3d_{5/2})$ can be observed up to 169 K. The peak became appreciably wider at 198 K when it underwent a significant attenuation. Above this temperature a large shift in the BE of $\text{I}(3d_{5/2})$ occurred from 620.6 eV to 619.9 eV. The position and intensity of the

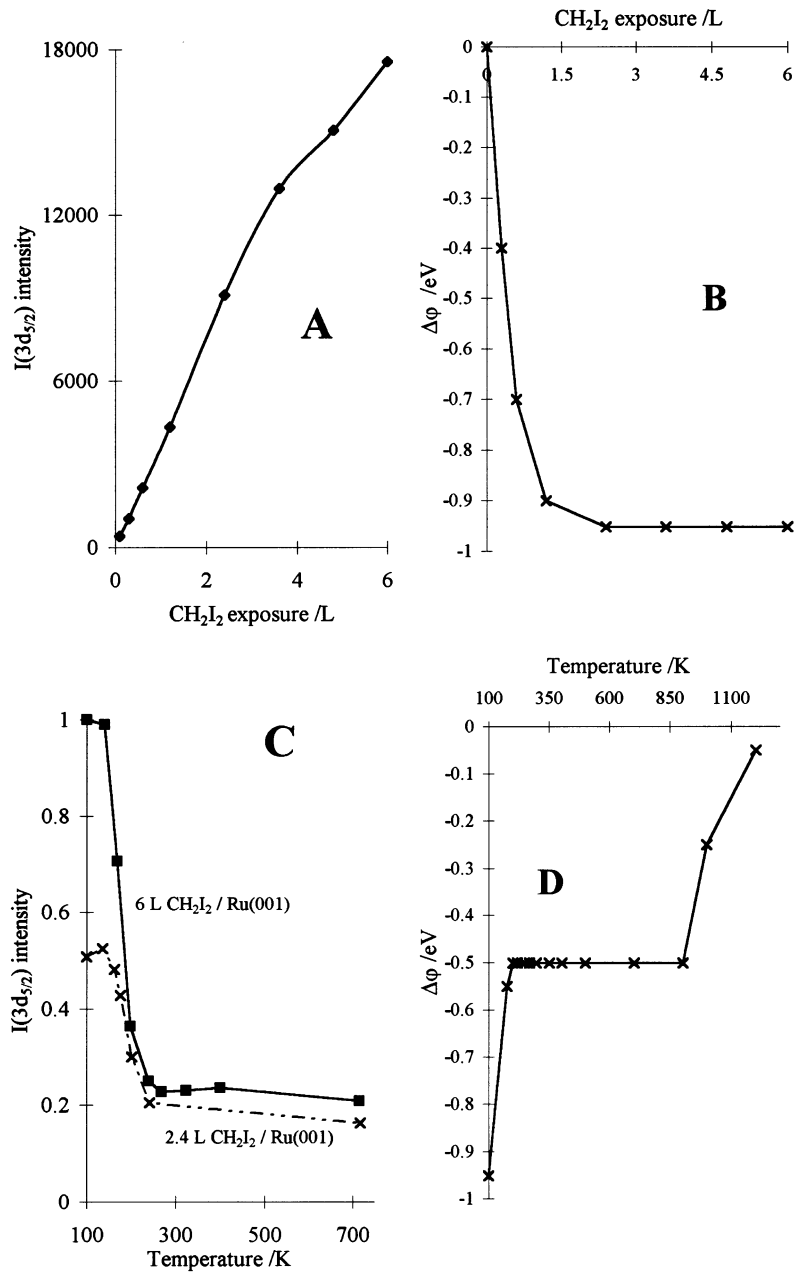


Fig. 2. (A) Area of the iodine XPS signal and (B) changes in the work function ($\Delta\phi$) of Ru(001) as a function of CH₂I₂ exposures at 110 K and (C, D) annealing temperature.

I(3d_{5/2}) signal remained unaltered above this temperature up to 900 K, the temperature of the onset of iodine desorption. Changes in the area of I(3d_{5/2}) peak are displayed in Fig. 2C.

Annealing the adsorbed layer caused an increase in the work function. A constant value was attained at 200 K. In this case the work function of the sample was about 0.5 eV lower than that

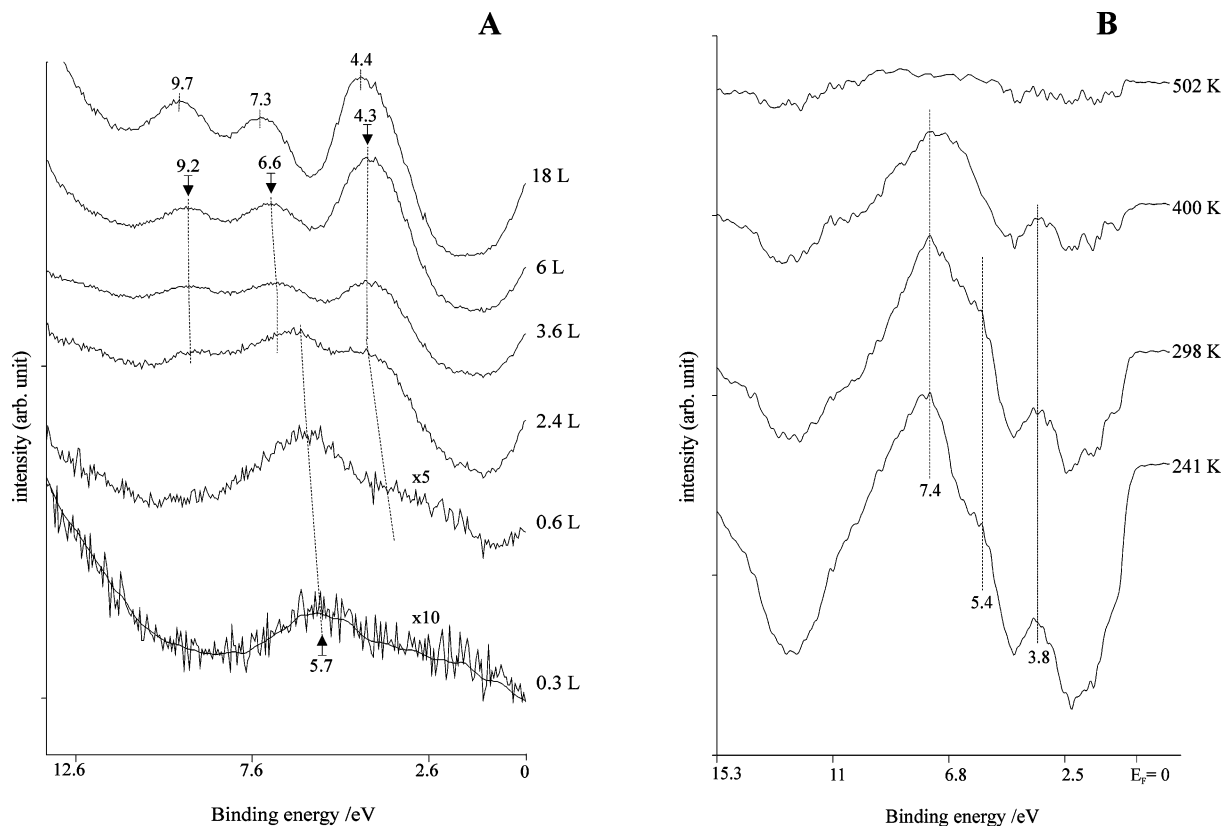


Fig. 3. HeI UP spectra of Ru(001) as a function of (A) CH_2I_2 exposure at 110 K and (B) annealing temperature for 6 L exposure of CH_2I_2 . In the latter case the spectrum registered after heating the adsorbed layer to 715 K was subtracted from each spectrum.

before CH_2I_2 adsorption. The next increase started at 850 K; the value characteristic of the clean surface was not attained even at 1200 K (Fig. 2D).

Table 1
UPS energies of species formed on metals following the adsorption of CH_2I_2

	UPS (eV)	Ref.
$\text{CH}_2\text{I}_2/\text{Pd}(100)$	4.0, 6.7, 9.2, 13.0	[17]
$\text{CH}_2\text{I}_2/\text{Cu}(100)$	3.9, 6.7, 7.4, 9.1, 13.2	[23]
$\text{CH}_2\text{I}_2/\text{Ru}(001)$	4.3, 6.6, 9.2, 13.0	(present work)
CH_2	5.8–6.2	[17]
	5.4–5.6	[23]
	5.5–5.8	[34]
	5.4	(present work)
I	5.5	[17]
	5.7	(present work)
CCH_3	7.6	[36]
	7.4	(present work)

The effect of annealing was also registered in the UP spectra of the adsorbed layer. Up to 200 K the spectra remained practically unaltered. At 241 K the dominant photoemission lines were at 5.7 and 4.5 eV, which were seen even after annealing the sample to 715 K, where — according to AES — only iodine and carbon were present on the surface. In order to identify the formation of other adsorbed species produced during annealing, the spectrum taken after heating the sample to 715 K was subtracted from each of the spectra taken at lower temperatures. The magnified difference spectra obtained in this way are displayed in Fig. 3B. For the sample annealed at 241 K, signals appeared at 3.8, 5.4 and 7.4 eV. The 5.4 eV peak disappeared only above 298 K, whereas the other two disappeared at 450–502 K.

By means of TPD we detected the following desorption products: CH_4 ($T_p=220$ K), H_2

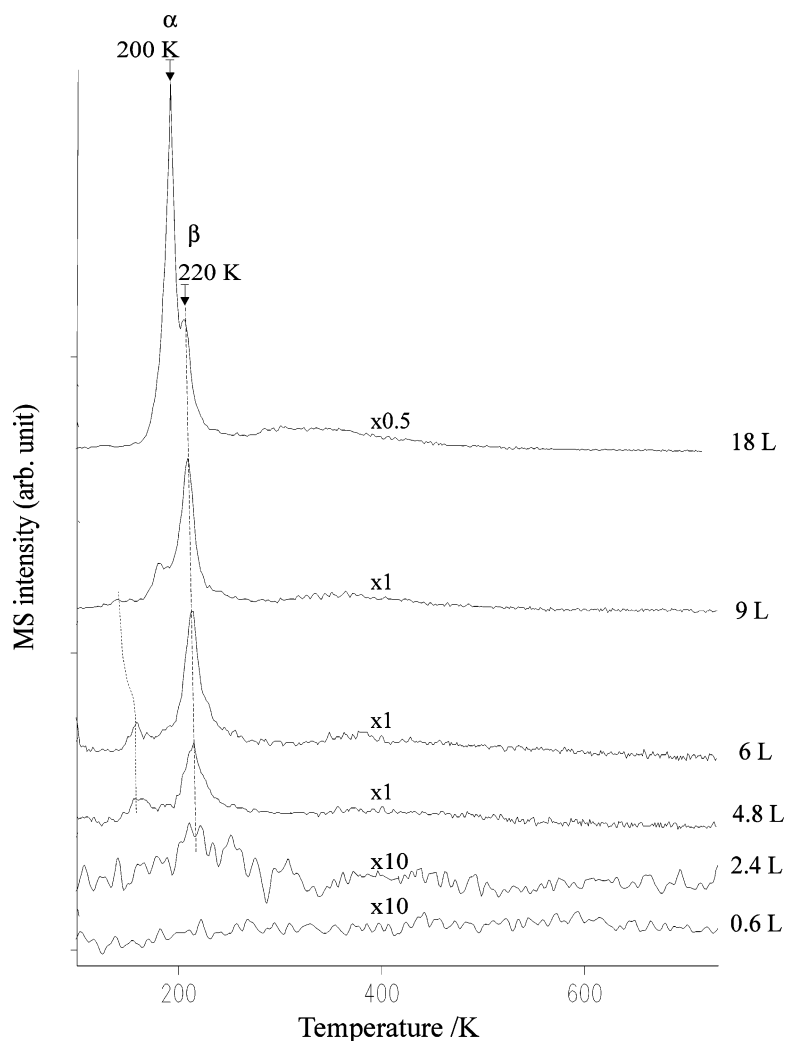


Fig. 4. Thermal desorption spectra of CH_2I_2 (amu 127) as a function of CH_2I_2 exposures. Adsorption temperature was 110 K.

($T_p=430$ – 420 K at lower exposures, $T_p=300$ and 430 – 450 K at higher exposures) and I ($T_p=1080$ – 1140 K). Note that the H_2 adsorbed from the background is released with $T_p=430$ K. Its amount is about one third of that measured after 0.3 L of CH_2I_2 exposure. In addition, we also found a peak for amu 142, which we identified as CH_3I . TPD spectra are presented in Fig. 5. It is important to note that we found no sign of ethylene formation following 27 and 28 amu. The activation energies for the desorption of these compounds were calculated by the Redhead formula assuming

a pre-exponential factor of $1 \times 10^{13} \text{ s}^{-1}$. Characteristic TPD data are collected in Table 2.

3.3. Effects of illumination

The primary aim of the illumination study was to promote the generation of CH_2 at low temperature (~ 100 K), where its decomposition and secondary reactions are minimal. The effect of illumination was exhibited by changes in the positions of the $\text{I}(3d_{5/2})$ in the XP spectra. Fig. 6 shows the effect of illumination time on the position of

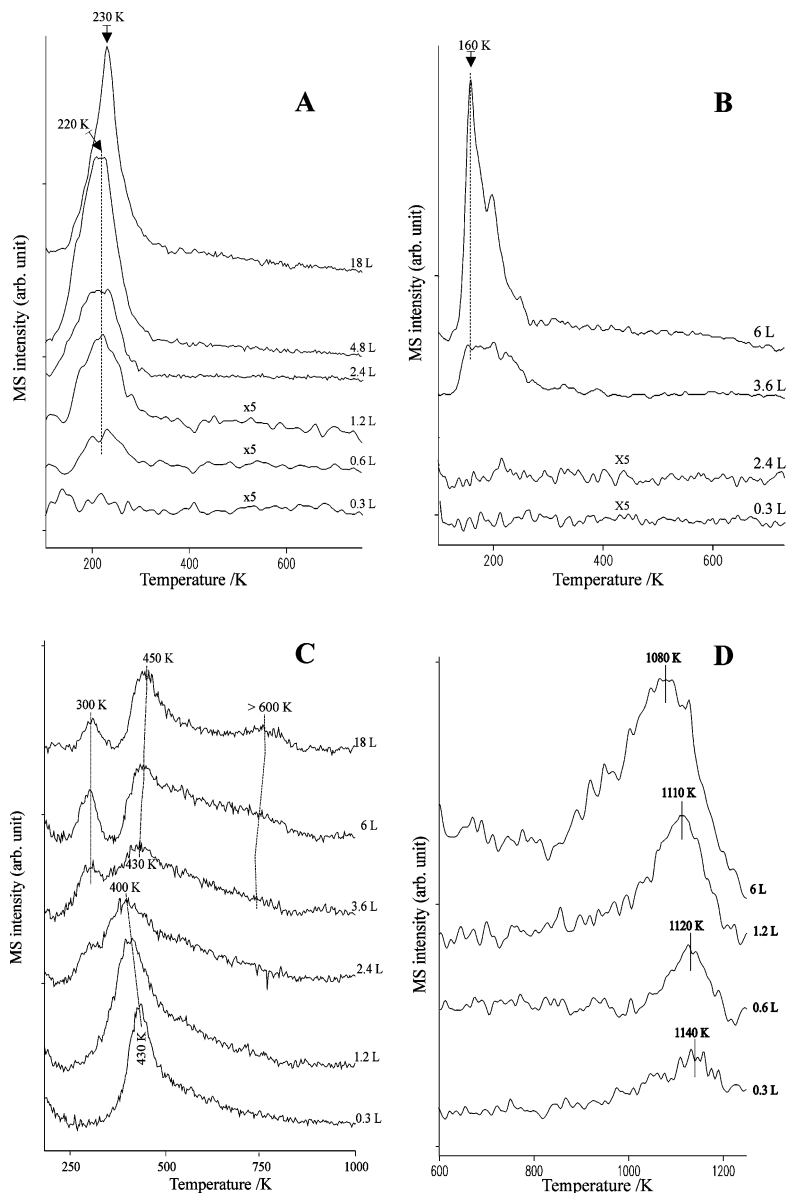


Fig. 5. Thermal desorption spectra for (A) CH_4 (amu 16); (B) CH_3I (amu 142); (C) H_2 (amu 2); (D) I (amu 127) as a function of CH_2I_2 exposure at 110 K.

the $\text{I}(3d_{5/2})$ peak at monolayer coverage. The BE value clearly shifted from 620.6 eV to 619.8 eV even after a relatively short (1–5 min) irradiation, which was also accompanied by a decrease of the peak area.

Illumination of the adsorbed layer caused a dramatic alteration in the HeI photoelectron

spectrum. After photolysis, photoemission signals characteristic of the adsorbed CH_2I_2 almost disappeared and a very intense signal appeared at 5.7 eV.

Post-irradiation TPD measurements for monolayer coverage showed that the amount of CH_2I_2 desorbed (β peak) decreased with increasing irradi-

Table 2
Some characteristic data for TPD. Data refer to monolayer coverage of CH₂I₂

	Desorption peak temperature T_p (K)	Activation energy E_a (kJ/mol) ^a
CH ₂ I ₂	220	63
CH ₃ I	160	46
CH ₄	220	63
I ⁺	1080	312
H ₂	300, 450, > 600	–

^a E_a was calculated by assuming first order kinetics ($k = 10^{13} \text{ s}^{-1}$).

ation time (Fig. 7A). No desorption of CH₂I₂ was detected after 60 min of illumination. The same is true for the desorption of CH₃I (Fig. 7B). In contrast, the irradiation hardly decreased the amount of methane and iodine produced. An interesting feature is that the amount of hydrogen desorbed above 400 K increased relative to that desorbed at lower temperature, $T_p = 300$ K. The peak temperature of H₂ desorption was shifted to higher values compared with the experiments without UV illumination. Great attention was paid to the detection of C₂H₂, C₂H₄ and C₂H₆, but none of them was found in the desorbing products.

4. Discussion

4.1. Adsorption of CH₂I₂

The adsorption of CH₂I₂ on Ru(001) surface caused a gradual decrease in the work function which reached a final value at ~ 3.0 L of CH₂I₂ exposure. The extent of the decrease is 0.96 eV, almost the same as measured for Pd(100) ($\Delta\phi = -0.85$ eV) [17] and Rh(111) ($\Delta\phi = -0.75$ eV) [18] surfaces. Much less change ($\Delta\phi \approx -0.1$ eV) was obtained for Cu(100) surface [23]. With regard to the bonding characteristics of adsorbed alkyl halides, it is very likely that CH₂I₂ bonds through the halogen atoms.

Following the uptake of CH₂I₂ by XPS measurements we found that the area of the I(3d_{5/2}) peak increased continuously with the rise of

CH₂I₂ exposure. As concerns the nature of the adsorption of CH₂I₂ at 110 K, the position of the I(3d_{5/2}) peak provides important information; the binding energy of I(3d_{5/2}) for atomically adsorbed I is always lower, 618.5–619.7 eV, than that for molecularly adsorbed iodo compounds, ≥ 620.5 eV [1–6]. From Fig. 1 the position of the I(3d_{5/2}) peak at very low exposure was 619.9 eV, and at higher exposures 620.6 eV. This latter value is characteristic of the molecularly adsorbed CH₂I₂. The lower value of binding energy for I(3d_{5/2}) suggests the occurrence of dissociation of CH₂I₂ at submonolayer at 110 K. From Fig. 1A we calculated that no more than 5% of a monolayer dissociates at 100 K.

Adsorption of CH₂I₂ on Ru(001) gave very weak photoemission signals in HeI photoelectron spectra at low coverage. At monolayer coverage (at an exposure of 6.0 L), when the position of the binding energy of I(3d_{5/2}) in the XPS suggested the presence of molecularly bonded CH₂I₂, photoemission peaks emerged at 4.4, 6.6, 9.2 and 13 eV. The position of these signals shifted to higher energies at multilayer coverage. If the gas-phase photoelectron spectrum of CH₂I₂ and the gas-phase ionization potentials are considered [32], the above peaks can be assigned to the (2b₁, 3b₂, 1a₂, 4a₁), (2b₂, 3a₁), 1b₁ and 2a₁ orbitals. The differences in binding energies in the adsorbed layer on Ru(001) approximate well to the values measured for gaseous CH₂I₂ [32]. From this finding, it may be concluded that the bonding of CH₂I₂ to Ru(001) did not result in a strong distortion of its molecular electronic structure.

As the analysis of XP spectra suggested the dissociation of CH₂I₂ at submonolayer coverage, great attention was paid to the UP spectra of these adsorbed layers. In the magnified difference spectra we observed a new photoemission line at 5.7 eV. In the UP spectra of polycrystalline Ni and Co, following the dissociative adsorption of CH₂I₂, a photoemission line at 5.5–5.8 eV was also detected [33]. This signal was also seen in the HeII photoelectron spectrum of adsorbed CH₂I₂ at submonolayer coverage on Pd(100) and Cu(100) surfaces [17,23]. In all these cases, this signal was attributed to adsorbed CH₂ species: this assignment is very likely valid in the present case, too.

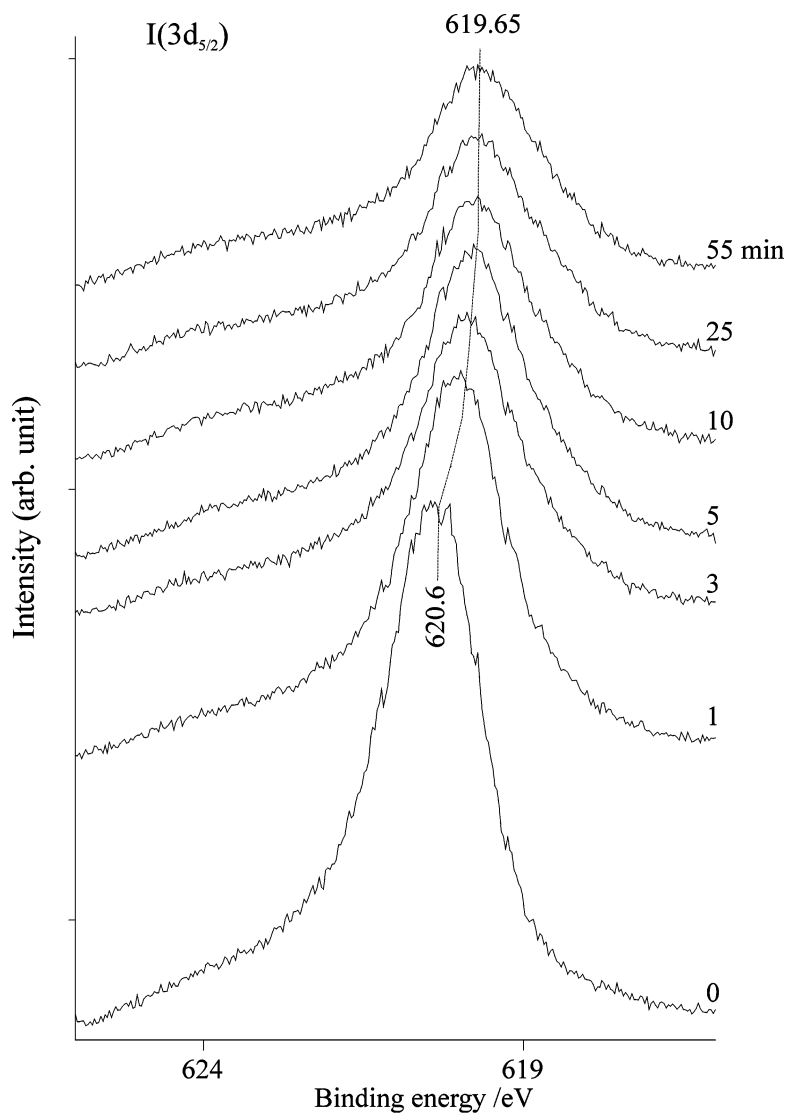


Fig. 6. Effects of illumination on the XP spectra of adsorbed CH_2I_2 on Ru(001) at 110 K. CH_2I_2 exposure was 6 L.

TPD measurements indicated two adsorption states denoted by β ($T_p=220$ K) and α ($T_p=200$ K). The β peak, which saturated at 6.0 L of CH_2I_2 exposure, represents the weakly adsorbed CH_2I_2 . As we could not obtain saturation of the α peak even at very high exposures, we may conclude that this peak corresponds to desorption of a multilayer. The value of T_p is nearly the same as determined for Rh(111) ($T_p=205$ K) and

Cu(100) ($T_p=210$ – 219 K). The surface coverage at monolayer calculated from TPD and XPS results is 8×10^{14} CH_2I_2 molecules/ cm^2 . The calculation was based on the comparison of the I($3d_{5/2}$) signal obtained for monolayer CH_2I_2 at 100 K with the XPS signal registered at saturation coverage of atomic iodine. Adsorbed iodine occupies one third of surface Ru atoms at saturation [34].

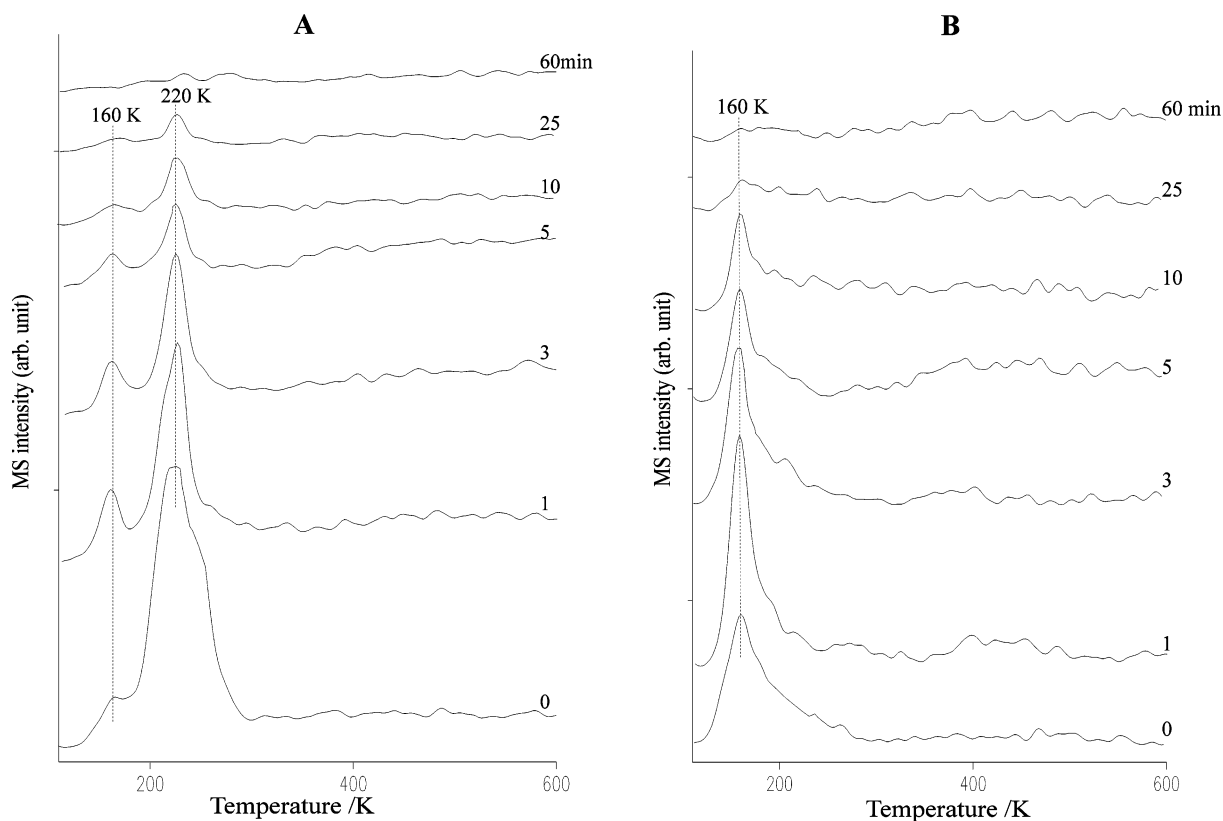
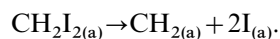


Fig. 7. Post-irradiation TPD spectra for (A) CH_2I_2 and (B) CH_3I , CH_2I_2 exposure was 6 L.

4.2. Annealing of adsorbed CH_2I_2

Spectroscopic results clearly showed that, in addition to the weakly adsorbed CH_2I_2 , a strongly bonded CH_2I_2 also exists on the surface, which dissociates at higher temperatures. According to the XPS measurements (Fig. 1B), this occurred by 198 K, where the $\text{I}(3d_{5/2})$ peak broadened and a shoulder could be distinguished at lower binding energy. The presence of this shoulder suggests that a fraction of the molecularly adsorbed CH_2I_2 underwent dissociation even at this temperature. At 239 K this shoulder became the dominant peak for $\text{I}(3d_{5/2})$, suggesting the completeness of the dissociation process

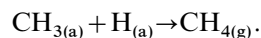
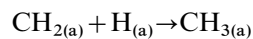
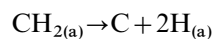


In the desorption products we found CH_4 ($T_p = 220$ K) and H_2 ($T_p = 300$ K and 430–450 K),

but could not detect ethylene, the product of the dimerization of adsorbed CH_2 . The formation of CH_4 suggests that the self-hydrogenation of CH_2

$$4\text{CH}_2 \rightarrow 2\text{CH}_4 + 2\text{C}$$

proceeds on $\text{Ru}(001)$. The emission at 4.5 eV in UP spectra above 200 K clearly shows the presence of $\text{C}_{(\text{a})}$ [33]. This process may consist of the following steps



We cannot exclude the possible assistance of hydrogen from the background to the above reactions.

The absence of ethylene in the desorbing gases is a somewhat surprising result as Ru is a good

catalyst for hydrocarbon synthesis. This behavior of Ru(001) resembles that of Rh(111) [18,19]. On Pd(100) we found a larger amount of C₂H₄ besides CH₄ [17], while on Cu surfaces only C₂H₄ was produced without CH₄ [23]. Careful examination of UP spectra revealed that after the desorption of weakly bonded CH₂I₂, at 205–210 K, weak photoemission signals at 5.7 and 7.4 eV remained in the magnified difference spectrum (Fig. 3B). The first is no doubt attributed to adsorbed CH₂ species. On the basis of previous study [35], the 7.4 eV signal can be ascribed to adsorbed ethylidyne, CCH₃. Accordingly, adsorbed CH₂ formed in the dissociation of CH₂I₂ above 173 K is coupled into ethylene, very likely in the di-σ-bonded form, which is converted into ethylidyne in a fast process



As has been demonstrated on several metal surfaces, the di-σ-bonded ethylene readily transforms into this species at 150–300 K [36–39].

Analysis of H₂ desorption curves is difficult due to the presence of hydrogen in the background. Although the extent of the adsorption of this hydrogen is certainly decreased at higher coverage of CH₂I₂, its contribution cannot be completely excluded, particularly at low CH₂I₂ coverage. The peak temperature for H₂ desorption following H₂ adsorption on clean Ru(001) is 430 K at low coverage, which is shifted to lower temperatures with increasing coverage [40,41]. This shift was also observed in our experiment (Fig. 5). In addition, a new H₂ peak developed with T_p = 300 K at higher surface concentration of CH₂I₂, very likely due to the influence of adsorbed iodine. It is known that coadsorbed species, like CO, forming a compressed overlayer shift the desorption temperature of H₂ to lower temperature [40]. The other peak for H₂ appeared at 440–450 K, which may correspond to the decomposition of ethylidyne



Although CCH₃ decomposes on Ru(001) surface at 300–350 K, the adsorbed species, in the present case the adsorbed iodine, can increase this temperature value by blocking the sites required for the surface decomposition. The CCH formed in the

above reaction is quite stable, it releases hydrogen only at 750 K (Fig. 5C).

An interesting feature of the CH₂I₂/Ru(001) system is the formation of CH₃I in the desorbing products with T_p = 160 K. This peak temperature agrees well with that registered following CH₃I adsorption on Ru(001) [42]. The production of this compound from adsorbed CH₂I₂ is rather unusual, it has been reported only on Al(111) surface [43]. The formation of methyl halide, CH₃Cl, was also observed following the adsorption of CH₂ClI on Pt(111), where the strength of the C–halogen bonds is obviously different [20].

As the formation of CH₃I occurred at higher CH₂I₂ coverages, when most of the active sites of the Ru surface are blocked, we may assume that it causes the adsorbed CH₂I₂ molecules to be tilted away from the surface normal as shown in Fig. 8. The CH₂I₂ bonds to the surface through the I atoms, but the structure of the (001) hcp plane and the equilibrium geometry of CH₂I₂ molecules do not fit perfectly. This ‘mismatching’ means that one of the iodine atoms of CH₂I₂ cannot occupy a site (presumably three-fold hollow sites) with the same binding energy. This is also reflected in the change of the work function, as Δφ reaches its minimum before the saturation of the first layer, approximately at 2.4 L, when CH₃I appeared in the desorption products. This is in harmony with the tilting mechanism, as the macroscopic dipole moment, and Δφ, depend on cos α, e.g. on the angle between the C₂ axis of the molecule and the surface normal [34]. The more molecules are on the surface, the larger is the tilting angle, with the results that (i) bonding I atoms are not equivalent and the CH₂I₂ molecule is in a stretched configuration, and (ii) the partially positive C atoms of CH₂I₂ become more open to nucleophilic reactants, such as surface H.

4.3. Photolysis of adsorbed CH₂I₂

Illumination of the adsorbed layer at 110 K caused a gradual shift in the position of I(3d_{5/2}) binding energy in XPS. After 10 min illumination time the peak attained a value of 619.65 eV, which is considered as a sign of the dissociation of CH₂I₂ to a great extent. At the same time the area

at low coverages



above 0.2 ML coverage

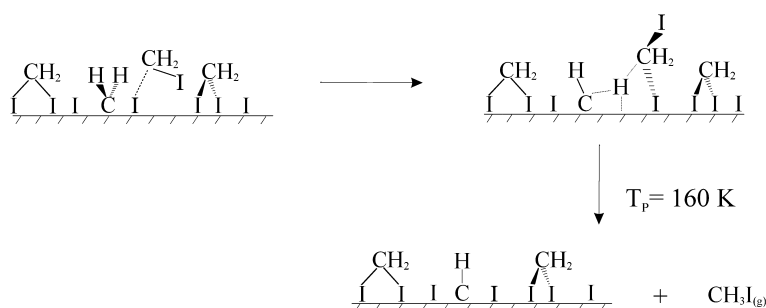


Fig. 8. Scheme for the adsorption and reaction of CH_2I_2 molecules and for the formation of CH_3I .

of the $\text{I}(3d_{5/2})$ signal decreased by 40%, indicating that a significant fraction of adsorbed CH_2I_2 underwent a photo-induced desorption (Fig. 6A). This conclusion is supported by the TPD results. The amount of CH_2I_2 desorbed around 220 K decreased and completely ceased after 60 min of illumination. A similar feature was observed for CH_3I desorption. In contrast, the formation of methane and iodine did not change, indicating that the extent of CH_2I_2 dissociation remained practically the same.

5. Conclusions

1. CH_2I_2 adsorbs dissociatively at submonolayer coverage on Ru(001) surface at 110 K, and molecularly at higher coverages.
2. The primary products of the dissociation are adsorbed CH_2 and I.
3. The majority of CH_2 is self-hydrogenated to CH_4 , a small fraction coupled into strongly bonded C_2H_4 , very likely di- σ -bonded form, which is converted immediately to ethynylidyne. This compound decomposed above 400 K.
4. Illumination of adsorbed CH_2I_2 with a Hg arc lamp enhanced the extent of dissociation even

at 110 K, but did not change the reaction pathway of adsorbed CH_2 .

Acknowledgements

This work was supported by the Hungarian Academy of Sciences (AKP 97-202,4) and by the Grant OTKA T23023.

References

- [1] F. Zaera, Acc. Chem. Res. 25 (1992) 260.
- [2] F. Zaera, J. Mol. Catal. 86 (1994) 221.
- [3] F. Zaera, Chem. Rev. 95 (1995) 2651.
- [4] B.E. Bent, Chem. Rev. 96 (1996) 1361.
- [5] F. Solymosi, in: E.G. Derouane et al. (Eds.), Catalytic Activation and Functionalism of Light Alkane, Kluwer Academic, Dordrecht, 1998, p. 369.
- [6] F. Solymosi, J. Mol. Catal. A: Chem. 131 (1998) 121.
- [7] X.-L. Zhou, J.M. White, Surf. Sci. 194 (1988) 438.
- [8] M.A. Henderson, G.E. Mitchell, J.M. White, Surf. Sci. 184 (1987) L325.
- [9] J.G. Chen, T.P. Beebe Jr., J.E. Crowell, J.T. Yates Jr., J. Am. Chem. Soc. 109 (1987) 1726.
- [10] A. Berkó, F. Solymosi, J. Phys. Chem. 93 (1989) 12.
- [11] X.-L. Zhou, P.M. Blass, K.C. Cannon, F. Solymosi, J.M. White, Surf. Sci. 219 (1989) 294.

- [12] F. Solymosi, J. Kiss, K. Révész, *J. Phys. Chem.* 94 (1990) 2224.
- [13] F. Solymosi, K. Révész, *J. Am. Chem. Soc.* 113 (1991) 9145.
- [14] K. Révész, F. Solymosi, *Surf. Sci.* 280 (1993) 38.
- [15] D. Jenz, M. Trenary, X.D. Peng, P.C. Stair, *Surf. Sci.* 341 (1995) 282.
- [16] X.D. Peng, R. Wiswanathan, G.H. Smudde, P.C. Stair, *Sci. Instrum.* 63 (1963) 3930.
- [17] F. Solymosi, I. Kovács, *Surf. Sci.* 296 (1993) 171.
- [18] G. Klivényi, F. Solymosi, *Surf. Sci.* 342 (1995) 168.
- [19] F. Solymosi, G. Klivényi, *J. Phys. Chem.* 99 (1985) 8950.
- [20] X.-L. Zhou, Z.-M. Lin, J. Kiss, D.W. Sloan, J.M. White, *J. Am. Chem. Soc.* 117 (1995) 3565.
- [21] J.-L. Liu, B.E. Bent, *J. Phys. Chem.* 96 (1992) 8529.
- [22] Ch.-M. Chiang, T.H. Wentzlaff, B.E. Bent, *J. Phys. Chem.* 96 (1992) 1836.
- [23] I. Kovács, F. Solymosi, *J. Phys. Chem.* 101 (1997) 5397.
- [24] X.-L. Zhou, J.M. White, *J. Phys. Chem.* 95 (1991) 5575.
- [25] C.W.J. Bol, C.M. Friend, *J. Am. Chem. Soc.* 117 (1995) 8053.
- [26] F. Solymosi, L. Bugyi, A. Oszkó, I. Horváth, *J. Catal.* 185 (1999) 160.
- [27] G. Wu, B.F. Bartlett, W.T. Tysoe, *Surf. Sci.* 373 (1997) 129.
- [28] M.K. Weldon, C.M. Friend, *Surf. Sci.* 321 (1994) L202.
- [29] H. He, J. Nakamura, J. Takehiro, K. Tanaka, *J. Vac. Sci. Technol. A* 13 (1995) 2689.
- [30] M.A. Henderson, P.L. Radloff, J.M. White, C.A. Mims, *J. Phys. Chem.* 92 (1988) 4111.
- [31] P.H. George, N.R. Avery, W.H. Weinberg, F.N. Tebbe, *J. Am. Chem. Soc.* 105 (1983) 1393.
- [32] W. van Niessen, L. Asbrink, G. Bieri, *J. Electron Spectrosc.* 26 (1982) 173.
- [33] F. Steinbach, J. Kiss, R. Krall, *Surf. Sci.* 157 (1985) 401.
- [34] T. Livneh, M. Asscher, *J. Phys. Chem. B* 101 (1997) 7505.
- [35] D.R. Lloyd, F.P. Netzer, *Surf. Sci.* 129 (1983) L249.
- [36] M.M. Hills, J.E. Parmeter, C.B. Mullins, W.H. Weinberg, *J. Am. Chem. Soc.* 108 (1986) 3554.
- [37] M.M. Hills, J.E. Parmeter, W.H. Weinberg, *J. Am. Chem. Soc.* 108 (1986) 7215.
- [38] C.M. Greenlief, P.L. Radloff, X.L. Zhou, J.M. White, *Surf. Sci.* 191 (1987) 93.
- [39] M.A. Henderson, G.E. Mitchell, J.M. White, *Surf. Sci.* 203 (1988) 378.
- [40] D.E. Peebles, J.A. Schreifels, J.M. White, *Surf. Sci.* 116 (1982) 117.
- [41] H. Shimizu, K. Christmann, G. Ertl, *J. Catal.* 61 (1980) 412.
- [42] Y. Zhou, M.A. Henderson, W.M. Feng, J.M. White, *Surf. Sci.* 224 (1989) 386.
- [43] M. Hasa, K. Pomen, M. Kato, T. Omishi, *J. Phys. Chem.* 96 (1992) 2637.