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THE DECOMPOSITION OF SURFACE METHOXY ON CLEAN AND OXYGEN POST DOSED Fe(100); CONTROL OF REACTION SELECTIVITY

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Pure methoxy overlayers on the Fe(100) surface were prepared and characterized by high resolution electron energy loss spectroscopy (HREELS). Reactions of the methoxy overlayer on the clean surface and in the presence of coadsorbed oxygen have been studied using temperature programmed reaction spectroscopy (TPRS). Post-dosed oxygen alters dramatically the selectivity of methoxy decomposition. Carbon monoxide and hydrogen are the major decomposition products from a pure methoxy overlayer, while formaldehyde is the major decomposition product from an oxygen coadsorbed methoxy overlayer. Clear evidence for production of formaldehyde via a disproportionation of methoxy is presented. Coadsorbed oxygen raises the decomposition temperature of methoxy by 200 K.

1. Introduction

Surface intermediates play a key role in chemical reactions on solid surfaces, most importantly in hetereogeneous catalytic reactions. The presence or stability of a particular intermediate often controls reaction yield or product selectivity. The isolation and investigation of surface intermediates is therefore important in elucidating surface reaction mechanisms. In addition, surface intermediates provide a unique class of chemical systems for fundamental studies.

In the decomposition of methanol (CH_3OH) on clean and modified transition metal surfaces, surface methoxy ($-OCH_3$) has been found to be an intermediate in most studies reported [1]. On many transition metal surfaces, such as Pd(100) [2], Ru(001) [3], Ni(111) [4], Ni(110) [5] and Mo(100) [6], methoxy decomposes at

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a surface temperature below the desorption of adsorbed hydrogen originating from CH_3O–H bond scission. On Cu and Ag single crystal surfaces, a significant amount of methoxy can be formed only in the presence of coadsorbed species, such as oxygen [7–11]. In the above mentioned systems, it is not possible to prepare a stable methoxy overlayer without coadsorbed species being present. On the Fe(100) surface, however, a pure surface methoxy overlayer can be prepared which is stable on the clean surface above the hydrogen desorption temperature [12,13].

Effects of preadsorbed oxygen on the decomposition reaction of methanol on Fe(100) have been reported [1,14]. However, in those studies the effects of oxygen on the decomposition of the methoxy intermediate are complicated by the steps leading to the formation of methoxy, which are also affected by preadsorbed oxygen. In the present work, a pure methoxy overlayer was prepared first and then exposed to oxygen, in order to study the effect of the post-dosed oxygen on methoxy decomposition. This approach simplifies the investigation of the effects of the coadsorbed species on the properties of the surface intermediate.

2. Experimental

The experiments reported here were carried out in a stainless steel ultrahigh vacuum (UHV) chamber, pumped by a 400 l/s ion pump, a 170 l/s turbomolecular pump, a Ti sublimator and a liquid nitrogen cooled trap. The chamber is equipped with multiple probes, such as a HREELS spectrometer, a quadrupole mass spectrometer for TPRS, a cylindrical mirror analyzer for Auger electron spectroscopy (AES) and a low energy electron diffraction (LEED) optics. The Fe(100) sample crystal is mounted on a manipulator with X, Y and Z linear motion and rotation. The temperature of the crystal is controlled by a combination of liquid nitrogen cooling and resistive heating. A K-type thermocouple is spot welded to the back of the crystal to monitor the crystal temperature.

The sample surface was cleaned by sputtering-annealing cycles. The cleanliness and ordering of the cleaned surface was checked by AES, HREELS and LEED. More detailed information on the cleaning procedure has been published [15]. After a clean and well ordered Fe(100) surface was prepared, it was exposed to methanol vapor at 103 K until a multilayer forms on the surface, as confirmed by TPRS spectra which showed a narrow and intense low temperature multilayer desorption peak. The methanol covered Fe(100) surface was then flashed to 373 K and cooled back to 103 K. The resulting overlayer consists of pure methoxy on the surface. This procedure for preparing a pure methoxy overlayer is based on our previous study of the CH_3OH/Fe (100) system [13].

Methanol used was Photorex grade liquid from Baker. It was loaded into a glass container attached to a gas/vapor manifold with a base pressure of 1×10^{-7} Torr. The liquid was dried over 3A molecular sieves (from Fisher) and degassed by freeze-pump thaw cycles [16]. Methanol vapor was dosed onto the Fe(100) surface through a doser, which consists of 0.25″ stainless steel tubing attached to a Varian adjustable leak valve. In order to minimize the background contamination by methanol vapor, the sample crystal was placed directly in front of the doser when dosing methanol and the background pressure was maintained below 1×10^{-9} Torr while dosing.

After methoxy/Fe(100) overlayers were prepared, they were characterized by HREELS and reactions of methoxy on the clean surface or in the presence of post-dosed oxygen were studied by TPRS. Oxygen used was a Matheson research purity (99.998%) gas. In the TPRS experiments, the sample crystal was heated resistively by a constant AC current. This resulted in a heating rate of approximately 10 K/s. Partial pressures of desorbing gases were monitored by an Inficon IQ-200 quadrupole mass spectrometer, interfaced to an IBM PC AT. Nine masses can be monitored in a single TPRS run. Intensity of TPRS spectra is based on the digital output from the mass spectrometer, with no calibration accounting for the relative sensitivity at different mass numbers performed. HREELS spectra were obtained with a MacAllister/RHK spectrometer. All spectra were recorded in the specular direction with an incident beam energy of 5 eV.

3. Results and discussion

Fig. 1 shows a typical HREELS spectrum for a pure methoxy overlayer on the Fe(100) surface. The vibrational peaks observed can be assigned as follows: M–OCH_3 stretch at 395 cm^{-1}; MO–CH_3 stretch at 1020 cm^{-1}; methyl deformation at 1430 cm^{-1}; symmetric C–H stretch at 2770 cm^{-1}; and asymmetric C–H stretch at 2880 cm^{-1}. There is a shoulder on the MO–CH_3 stretching peak, perhaps originating from the methyl rocking mode whose frequency is around 1124 cm^{-1} [17]. No O–H stretching band (around 3259 cm^{-1}) or O–H out-of-plane bending mode (around 750 cm^{-1}) can be observed. A more detailed discussion of the peak assignments has been published [1,13]. TPRS spectra of this methoxy overlayer are shown in fig. 2. The desorption of CH_3OH molecules was monitored by mass 31, the highest intensity fragment of the CH_3OH spectra [18]. The desorption of H_2CO was monitored by mass 30. The mass 30 intensity also contains a small portion of CH_3OH fragmentation, which is about 5% of the intensity at mass 31, as determined by the relative intensities of mass 30 and mass 31 resulting from multilayer methanol desorption. Masses 28, 18 and 2 reflect the desorption of CO, H_2O and H_2, respectively. As seen from fig. 2, the major reaction products are H_2 and CO for methoxy decomposition on the clean surface. Only a small amount of H_2CO and CH_3OH can be detected. There are two desorption peaks for CO, one around 440 K and the other around 800 K. The higher temperature peak originates from the recombination of atomic C and O, resulting from the total decomposition of methoxy on the surface. The lower

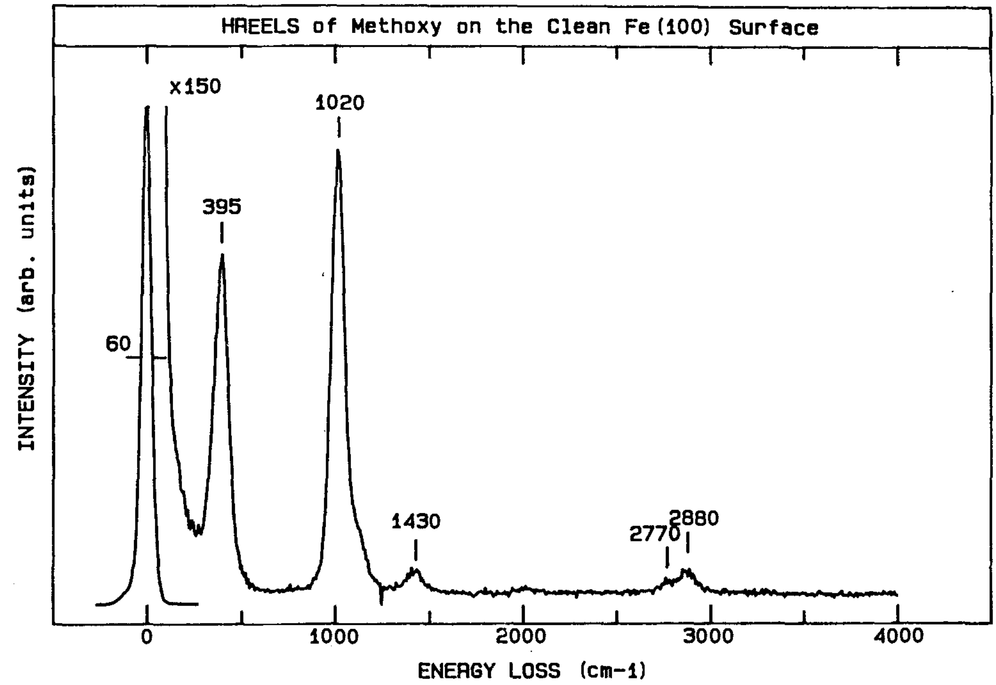

Fig. 1. HREEL spectrum of the methoxy overlayer on the clean Fe(100) surface.

temperature peak at 400 K results from the decomposition of methoxy without CO bond scission [1,13]. Although the desorption peak temperatures for H_2 and CO separately from the clean Fe(100) surface are significantly different [19], the H_2 peak and the lower temperature CO peak from the decomposition of methoxy on the clean Fe(100) surface fall into the same temperature region, indicating that the two reaction products originate from the same rate-limiting reaction step [20].

If this pure methoxy overlayer is exposed to oxygen, the reaction of methoxy is modified dramatically. Fig. 3 shows a HREELS spectrum taken after a methoxy overlayer is exposed to 10 L O_2 ($1\ L = 1 \times 10^{-6}$ Torr · second). Compared with the HREELS spectrum of the pure methoxy overlayer (fig. 1), the spectrum shows somewhat poorer resolution and a lower counting rate. (The typical counting rate of the elastic peak from an oxygen coadsorbed overlayer is $5x10^4$ counts per second, while the counting rate for a pure overlayer is greater than 1×10^5 counts per second). The M–OCH_3 is now embedded in a broad band around 500 cm^{-1}, which can be attributed to the combination of M–O stretching [15] and M–OCH_3 stretching (fig. 1). The assignment for the other peaks in fig. 3 is similar to that of fig. 1.

TPRS spectra of the oxygen coadsorbed overlayer are shown in fig. 4. In contrast to the case of the pure methoxy overlayer, the formation of H_2 and CO is restricted by post-dosed oxygen. On the other hand, a significant amount of H_2CO and CH_3OH is formed. Two CH_3OH desorption peaks are observed. The

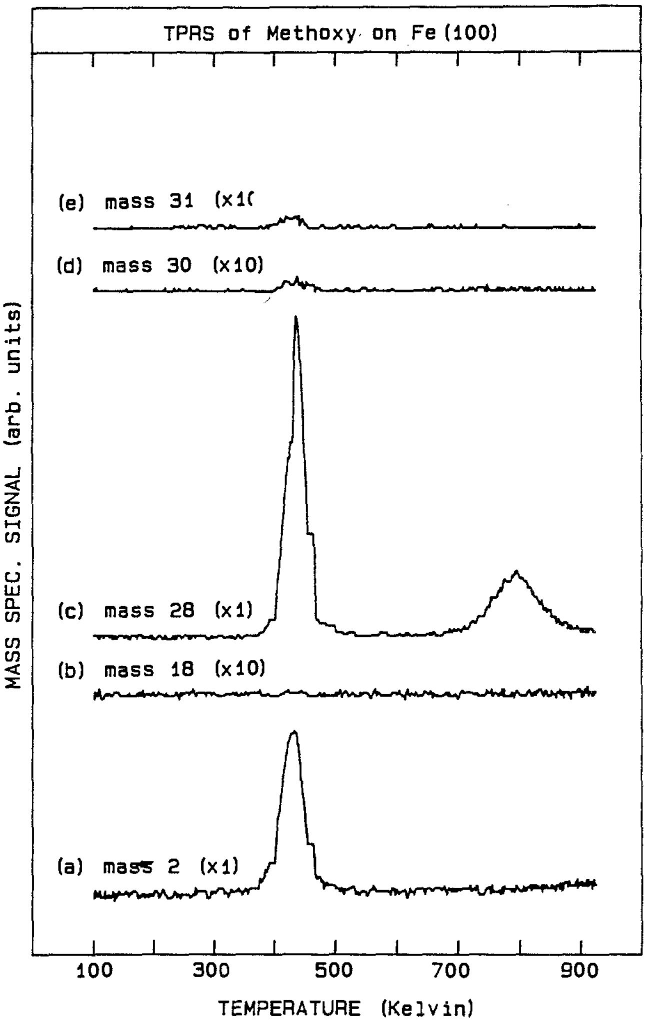

Fig. 2. TPRS of the surface methoxy overlayer on the clean Fe(100) surface.

origin of the lower temperature peak is not clear at present. It may result from the reaction of surface methoxy with hydrogen from ambient, or it may be due to the adsorption of molecular CH_3OH replaced by O_2 from the doser walls. Because this work focussed on the decomposition of methoxy, no further experiments were performed to clarify the origin of the lower temperature methanol desorption peak. The higher temperature CH_3OH peak falls in the same temperature region as the H_2CO peak. Both of these products result from the same reaction step. This step is likely to be the disproportionation of surface methoxy:

$$CH_3O_{(ad)} + CH_3O_{(ad)} \rightarrow H_2CO_{(g)} + CH_3OH_{(g)}$$

The small amount of water desorption at slightly higher temperature suggests that

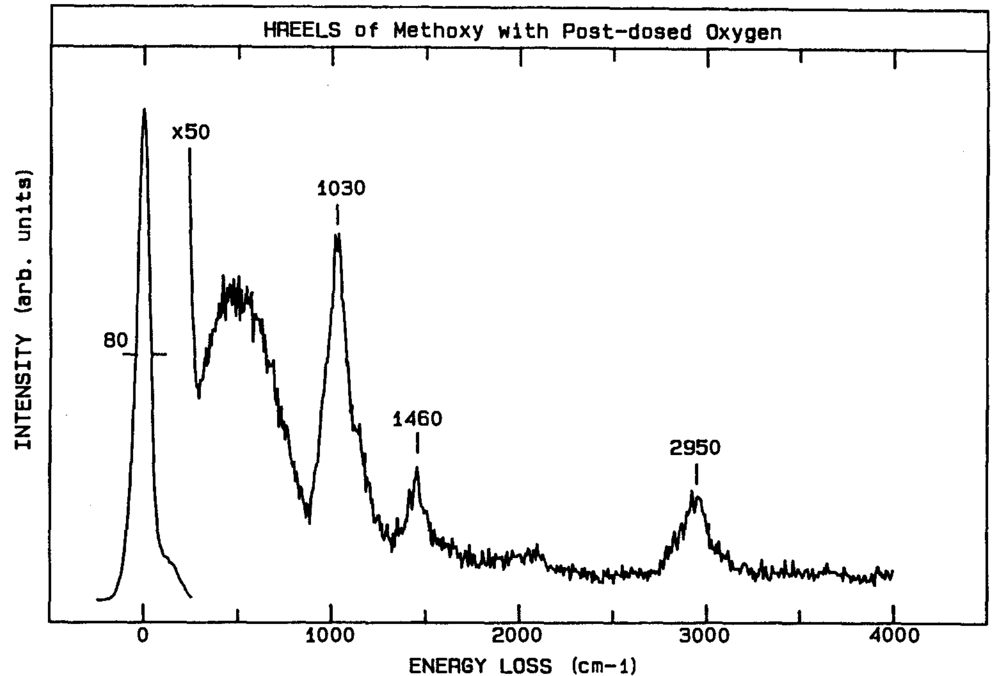

Fig. 3. HREEL spectrum taken after exposing the $CH_3O/Fe(100)$ overlayer to 10 L O_2 at 103 K.

a further channel for the production of formaldehyde may be the reaction of methoxy with adsorbed oxygen

$$CH_3O_{(ad)} + O_{(ad)} \rightarrow H_2CO_{(g)} + OH_{(ad)}$$

The adsorbed OH may then react further with methoxy or background hydrogen to form water.

The results presented above show that the reaction of methoxy is very different with or without post-dosed oxygen. The major C containing decomposition product is CO from a pure methoxy overlayer, while the major C containing decomposition product is H_2CO from an oxygen coadsorbed methoxy overlayer. By comparing the formation of CO and H_2CO in the two different cases, the effects of post-dosed oxygen can be seen more clearly. Fig. 5 shows the TPRS spectra of the CO and H_2CO products for the two cases. It can be seen that the selectivity of the methoxy decomposition is dramatically modified, and that the methoxy decomposition temperatures are very different. The decomposition of methoxy occurs 200 K higher for the oxygen coadsorbed overlayer than for the pure overlayer, indicating a much higher thermal stability of methoxy on an oxygen coadsorbed surface. The formation of H_2CO takes place primarily through the disproportionation of surface methoxy. C–H bond scission, a necessary step for methoxy to decompose, apparently does not occur via interaction directly with the substrate surface, but rather through interaction with another surface

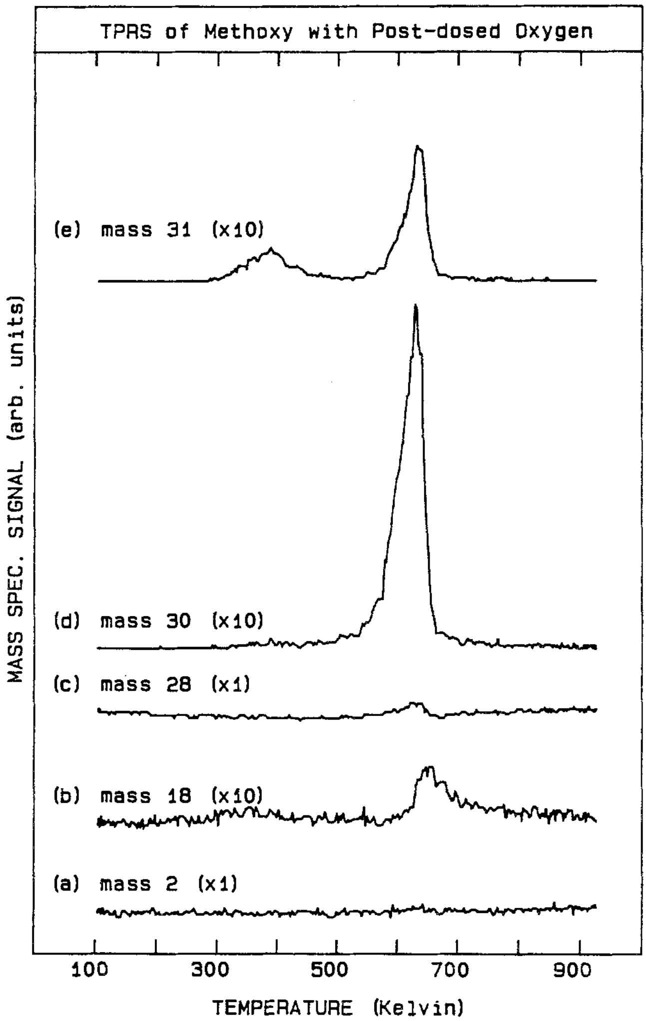

Fig. 4. TPRS of surface methoxy with post-dosed oxygen on the Fe(100) surface.

methoxy or adsorbed oxygen. Coadsorbed oxygen thus reduces the overall activity of the surface towards C–H bond scission and enhances the thermal stability of the surface methoxy.

In previous studies of methanol decomposition on oxygen preadsorbed Fe(100) [1,14], the effects of coadsorbed oxygen on the methoxy intermediate are complicated by reaction steps preceding the methoxy decomposition step. In the present work, a different approach has been applied, which more clearly identifies the role of coadsorbed oxygen on the decomposition of the methoxy intermediate.

In summary, post-dosed oxygen blocks the methoxy decomposition pathway leading to the formation of CO, while enhancing the formation of H_2CO. This apparently occurs by way of the disproportionation of methoxy, producing

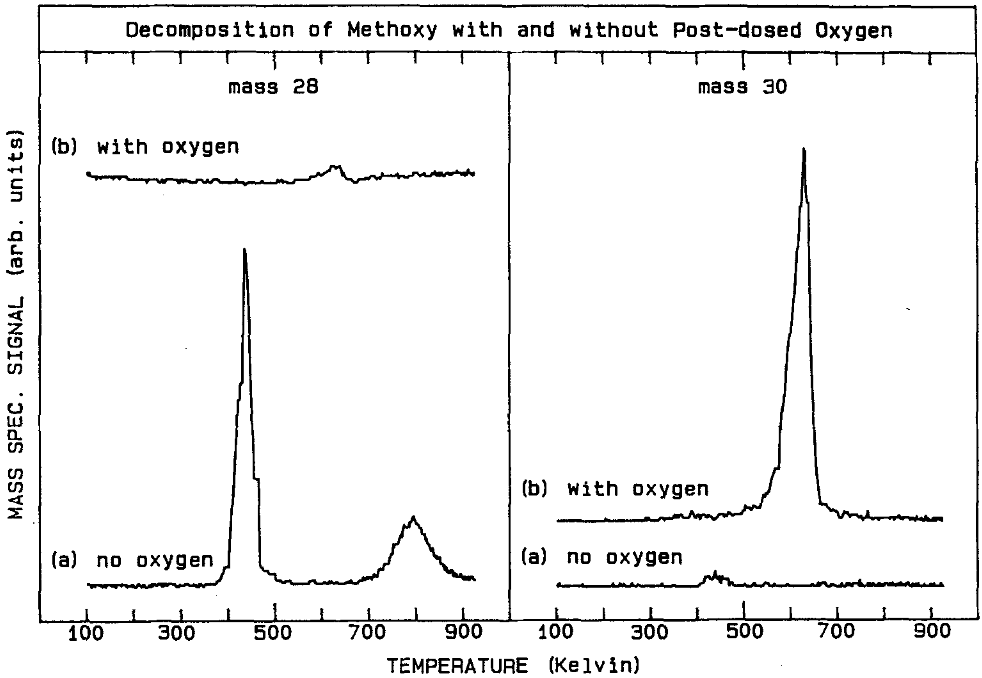

Fig. 5. Formation of CO (left) and H_2CO (right) from temperature programmed reaction (TPR) of methoxy without (a) and with (b) post-dosed oxygen.

formaldehyde as the principal decomposition product. Smaller amounts of molecular methanol and water are formed in the same reaction process. The activity of an Fe(100) surface towards the breaking of C–H bonds is evidently reduced by the presence of oxygen. This approach to the isolation and investigation of surface intermediates is helpful in understanding complex surface reaction mechanisms.

Acknowledgements

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References

[1] J.P. Lu, M.R. Albert, S.L. Bernasek and D.J. Dwyer, Surf. Sci. 218 (1989) 1.
[2] K. Christmann and J.E. Demuth, J. Chem. Phys. 76 (1982) 6318.
[3] J. Hrbek, R.A. DePaola and F.M. Hoffmann, J. Chem. Phys. 81 (1984) 2818.
[4] J.E. Demuth and H. Ibach, Chem. Phys. Lett. 60 (1979) 395.
[5] S.R. Bare, J.A. Stroscio and W. Ho, Surf. Sci. 150 (1985) 399.

[6] S.L. Miles, S.L. Bernasek and J.L. Gland, J. Phys. Chem. 87 (1983) 1626.
[7] J.N. Russell, Jr., S.M. Gates and Y.T. Yates, Jr., Surf. Sci. 163 (1985) 516.
[8] I.E. Wachs and R.J. Madix, J. Catal. 53 (1978) 208.
[9] M. Bowker and R.J. Madix, Surf. Sci. 95 (1980) 190.
[10] B.A. Sexton, A.E. Hughes and N.R. Avery, Surf. Sci. 155 (1985) 366.
[11] I.E. Wachs and R.J. Madix, Surf. Sci. 76 (1978) 531.
[12] J.B. Benziger and R.J. Madix, J. Catal. 65 (1980) 36.
[13] M.R. Albert, J.P. Lu, S.L. Bernasek and D.J. Dwyer, Surf. Sci. 221 (1989) 197.
[14] J.P. Lu, M.R. Albert, S.L. Bernasek and D.J. Dwyer, Decomposition of methanol on oxygen modified Fe(100), Part-II, Surf. Sci., submitted.
[15] J.P. Lu, M.R. Albert, S.L. Bernasek and D.J. Dwyer, Surf. Sci. 251 (1989) 348.
[16] D.D. Perrin and W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed. (Pergamon Press, Oxford, 1988).
[17] M. Falk and E. Whalley, J. Chem. Phys. 34 (1961) 1554.
[18] S.R. Heller and G.W.A. Miline, *EPA/NIH Mass Spectral Data Base*, Vol. 1 (NSRDS, 1978).
[19] J.B. Benziger and R.J. Madix, Surf. Sci. 94 (1980) 119.
[20] R.J. Madix, CRC Crit. Rev. Solid State Mat. Sci. 7 (1978) 143.