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The Adsorption and Decomposition of Methanol on Fe(110) Studied by Auger Electron Spectroscopy

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Electron impact-induced carbon Auger spectra of methanol adsorbed on Fe(110) are reported. The fine structure in the carbon Auger spectrum allows a distinction to be made among chemisorbed methanol, multilayer physisorbed methanol, and an adsorbed methoxy species formed on thermal decomposition of the adsorbate at 200 K. Further thermal decomposition occurs above 350 K to eventually give adsorbed carbon atoms. The differentiated Auger spectrum of the adsorbed methoxy species, CH_3O^-, bears a striking similarity to that reported previously for the adsorbed ethylidyne species $CH_3—C\equiv$. © 1988 Academic Press, Inc.

INTRODUCTION

The identification of adsorbed species that arise from the decomposition of molecular adsorbates, or from reactions between coadsorbed species, is important in studies that seek to establish the stability of surface species believed to be intermediates in catalytic processes.

The carbon, nitrogen, and oxygen Auger spectra of adsorbates have been shown to be useful "fingerprints" of the adsorbed species (*1–4*). These spectra may be excited by X rays (XAES) (*1, 2*) or electron impact (*3, 4*). X-ray excitation leads to rather weak spectra, and therefore requires long accumulation times, but unwanted decomposition or desorption of the adsorbate is slight and easily controlled. For electron impact excitation the incident current can be adjusted to give good-quality spectra in tens of seconds but great care needs to be taken to ensure that electron impact-induced decomposition or desorption occurs to a negligible extent. It has been shown that this may readily be achieved when studying chemisorbed species such as unsaturated hydrocarbons or carbon monoxide by using incident electron fluxes of the order of 0.1 $\mu A\ mm^{-2}$ (*1*) and recording spectra in a few minutes. More weakly chemisorbed species and physically adsorbed molecules are found to be more susceptible to electron beam damage and hence present greater difficulties for study by electron impact-induced AES.

In this paper we report Auger spectra of methanol adsorbed on Fe(110) both before and after thermal decomposition. Adsorbed methanol is known to be highly electron beam sensitive (*2*) and so rather short recording times were used. Nevertheless, we demonstrate that useful chemical information can be obtained from AES studies under these conditions and we report an Auger "fingerprint" for the adsorbed methoxy species found as an intermediate in the thermal decomposition of adsorbed methanol.

METHODS

A VG ESCA3 electron energy analyzer was mounted in a diffusion-pumped vacuum chamber with base pressure 2×10^{-11} torr. The data were recorded, stored, and displayed using a VGS 1000 data system. The iron crystal was cleaned by argon ion bombardment and annealing at 1100 K.

The spectrometer was operated in a con-

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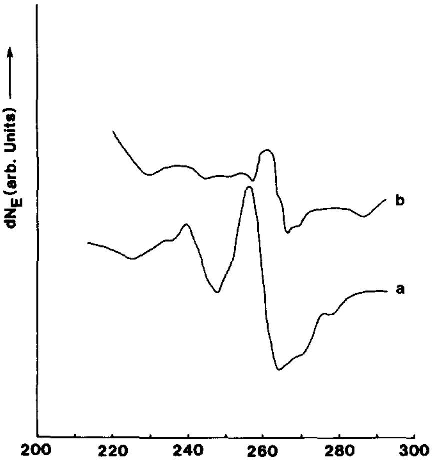

FIG. 1. Carbon dN_E Auger spectra of a clean Fe(110) surface exposed to methanol at 100 K. (a) 3 L, (b) 0.3 L.

stant (100 eV)-pass energy mode giving 2 eV resolution. A modulation voltage of 1 eV peak-to-peak was used to record dN_E spectra which were digitally integrated to give the corresponding N_E spectra. There are two advantages in recording spectra in the differential mode: first, there is more fine structure in the "fingerprint"; second, it is possible to use a higher beam current because the channeltron multiplier is operated well below its saturation voltage and can tolerate higher currents. To record spectra directly in the N_E mode a beam current of $<10^{-8}$ A would have to be used to keep the total count rate below $\sim 10^5$/s and it would be necessary to accumulate spectra over a much longer time to achieve a reasonable signal-to-noise ratio.

A beam current of 0.5 μA, 3 keV irradiating an area ~2–3 mm in diameter was used to excite the Auger spectra. This corresponds to an incident electron flux of approximately 0.1 μA mm^{-2}. For each adsorption temperature a series of carbon Auger spectra were recorded over time intervals ranging from 12 to 200 s to determine the time required for noticeable electron beam damage of the adsorbate. The spectra presented in this paper were recorded within this time limit with the exception of that of multilayers of methanol. In that case it was found that noticeable beam damage, in the form of peak broadening, occurred following less than 12 s exposure to the electron beam (<1.2 C m^{-2}). For the chemisorbed species spectra were recorded here for 50 or 100 s without noticeable beam damage.

Dry methanol was further purified by repeated freeze–pump–thaw cycles and checked for purity mass spectroscopically in the UHV chamber before it was used as the adsorbate.

During adsorption all the filaments in the spectrometer chamber were switched off and the pressure was monitored using a remote pressure gauge mounted just above the diffusion pump. Consequently, the actual exposures were higher than those quoted.

RESULTS

Two distinct lineshapes of carbon Auger spectra, one characteristic of low exposures (≤ 0.3 L) and the other characteristic of high exposures, were observed, as shown in Fig. 1, for methanol adsorbed on a

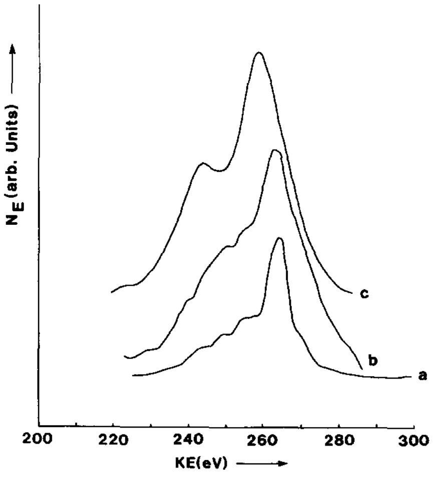

FIG. 2. Carbon N_E Auger spectra. (a) Gas-phase methanol. (b) Fe(110) exposed to 0.3 L methanol at 100 K. (c) Fe(110) exposed at 3 L methanol at 100 K.

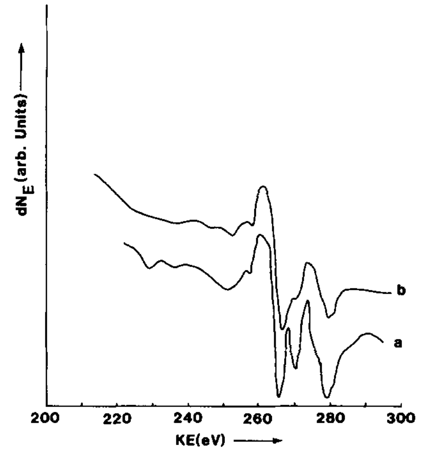

FIG. 3. Carbon dN_E Auger spectra of Fe(110) exposed to methanol at 300 K. (a) 0.5 L. (b) Saturated.

clean Fe(110) surface at 100 K. Increase in exposure gradually transforms the low exposure spectrum to the high-exposure spectrum. The corresponding N_E spectra are shown in Fig. 2. The dN_E spectrum of methanol at low coverage has its main peak (negative deflection) at 266 eV and shows a number of minor peaks and shoulders, while the high-coverage dN_E spectrum is dominated by two main peaks at 264.5 and 247 eV. This distinction is again clear in the N_E spectra (Fig. 2), where the main peak positions are 263 eV at low exposure and 259 and 242 eV at high exposure.

The carbon Auger spectrum of a clean Fe(110) overface exposed in 0.5 L of methanol at room temperature (300 K) (Fig. 3a) has three major peaks at 279, 271, and 266 eV. Increasing the exposure beyond 0.5 L causes some loss of definition in the spectrum and loss of intensity in the 271-eV peak. The corresponding spectra after integration are shown in Fig. 4.

The carbon dN_E Auger spectra obtained when a clean Fe(110) surface saturated with methanol at 100 K was heated to higher temperatures are shown in Fig. 5. The corresponding N_E spectra are shown in Fig. 6. Each spectrum shown was obtained by slowly raising the temperature of a clean Fe(110) surface saturated with methanol at 100 K to the required temperature and holding the crystal at that temperature for 5 min before cooling to 100 K to record the Auger spectrum. In a separate experiment the Fe(110) surface saturated with the adsorbate at 100 K was held at the required temperature while the Auger spectrum was recorded. The two above-mentioned procedures yielded similar spectra.

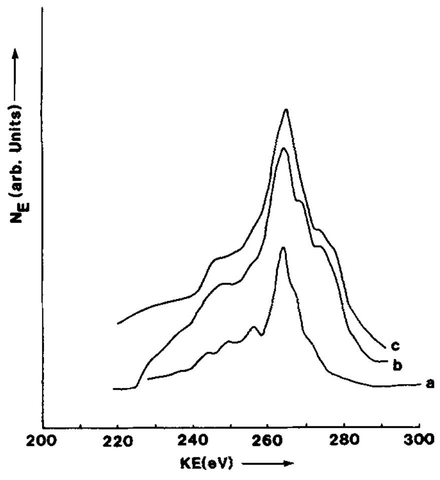

FIG. 4. (a) Carbon N_E Auger spectra of gas-phase dimethyl ether. (b) Fe(110) exposed to 0.5 L methanol at 300 K. (c) Fe(110) saturated with methanol at 300 K.

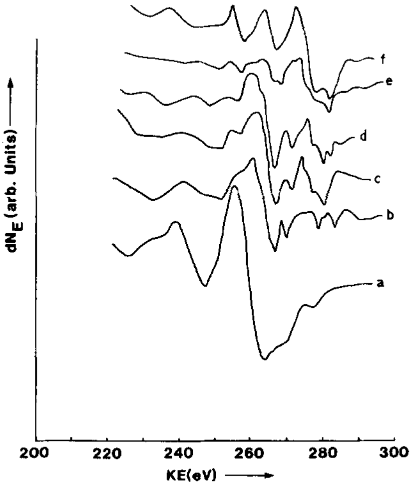

FIG. 5. Thermal evolution of the carbon dN_E Auger spectrum of Fe(110) saturated with methanol at 100 K. (a) 100 K. (b) 200 K. (c) 295 K. (d) 350 K. (e) 380 K. (f) 550 K.

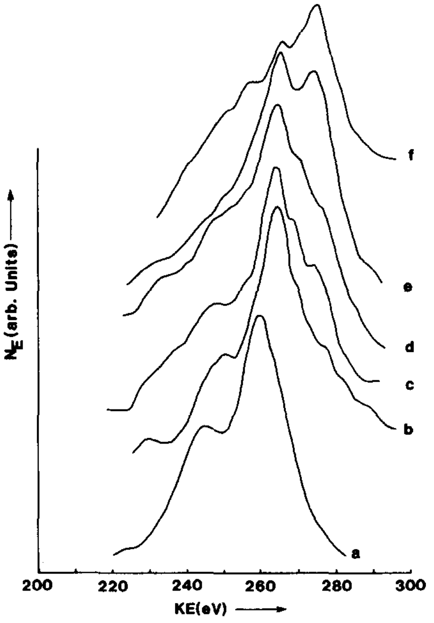

FIG. 6. Thermal evolution of the carbon N_E Auger spectrum of Fe(110) saturated with methanol at 100 K. (a) 100 K. (b) 200 K. (c) 295 K. (d) 350 K. (e) 380 K. (f) 550 K.

DISCUSSION

The N_E spectrum of methanol adsorbed at low coverage, presumably submonolayer, is compared with that of gas-phase methanol in Fig. 2. The carbon Auger spectrum of methanol gas has been described as "methane-like" (*5*) because it retains the main Auger features involving the higher energy t_2 triply degenerate molecular orbitals of methane (which contribute to the major peak) and the lower energy a_2 orbital (which contributes to the lower energy, smaller peaks). The reason for this similarity is that carbon Auger emission from methanol will be dominated by molecular orbitals with significant amplitudes near the carbon 1*s* hole, and these will be similar to those in methane. In addition there are some features, such as the high-energy shoulder in Fig. 2a, that are not observed in the methane spectrum and are associated with Auger emission involving molecular orbitals centered largely on the substituent, OH (*5*).

While there are some similarities in the disposition of peaks in the adsorbed phase and gas phase, the spectrum of the adsorbate is much broader. The gas spectrum has been shifted upward by 14 eV to align the major peak with that of the adsorbate spectrum. Approximately 5 eV of this shift is associated with the different reference levels (vacuum level for the gas spectrum, Fermi level for the adsorbate), while the remainder, 9 eV, is largely due to stabilization of the doubly charged final state by polarization of its surroundings. This latter shift, known as a relaxation shift, is typically 14–15 eV for the carbon Auger spectrum of chemisorbed species such as ethylene or carbon monoxide (*3*, *4*). In the case of first-layer methanol, although this can be regarded as chemisorbed, the valence electrons involved in the carbon Auger transitions tend to be localized on the methyl group and have little metal character. As a result the relaxation shift is more typical of a physically adsorbed molecule such as ethane (*4*).

The spectrum resulting from the higher exposure to methanol (Fig. 2c) resembles that of a thick layer of condensed methanol (*2*). The extra peak at 242 eV has been associated with a shake-off process identified in the energy-loss spectrum of solid methanol (*2*). Note that the relaxation-plus-work function shift is 4 eV lower than for chemisorbed methanol. According to the previous study of solid methanol by both electron and X-ray excited AES, broadening of the spectrum arises from electron beam damage and becomes noticeable at electron irradiation doses above 2.5×10^{-4} C cm^{-2} at 1500 eV beam energy. The spectrum in Fig. 2c was measured with a total electron dose of 6×10^{-4} C cm^{-2} at 3 keV and so it is likely that some significant damage has occurred. There have been no previous AES studies of submonolayer methanol but our results suggest that the spectrum in Fig. 2b has not been affected by electron beam damage. We would also expect chemisorbed methanol to have a significantly lower cross section for damage, compared with solid methanol, because of relaxation pathways involving energy transfer to the metal.

The spectrum resulting from methanol adsorption at 300 K (Fig. 4b) differs from the low-temperature spectrum mainly in the appearance of two high-energy peaks, one broad and centered at ~275 eV and another at 269 eV. Also, there is a small upward shift in the main peak position, which may be due to an increased relaxation shift. Here we note that in studies of Auger spectra in the gas phase, change in the environment of the methyl group in methanol on passing to dimethyl ether has been found to result in little change in the carbon Auger spectrum except for the appearance of a stronger shoulder above the main peak (*5*). We show the dimethyl ether gas spectrum for comparison (Fig. 4a). By analogy we suggest that the changes we observe in the spectrum at 300 K result from conversion from methanol to a surface methoxy species. The broad shoulder centered at 275 eV has no counterpart in the gas-phase spectrum of either methanol or dimethyl ether; this probably results from Auger emission from valence orbitals with significant oxygen $2p$ and metal $3d$ character but with sufficient carbon character to contribute to the carbon Auger spectrum.

The spectrum resulting from higher exposure to methanol at 300 K shows some loss of fine structure which may result from some adsorption of undissociated methanol.

On heating the multilayer of methanol adsorbed at 100 K (Figs. 5 and 6), it is clear that decomposition to adsorbed methoxy species has begun at 200 K. The methoxy species is stable to 350 K but substantial decomposition to a species where carbon is bound directly to the metal has occurred by 380 K; this is apparent from the increased intensity at 275 eV in the N_E spectrum. The spectrum has changed to that of adsorbed carbon atoms at 550 K.

CONCLUSIONS

Auger electron spectroscopy has been used to distinguish monolayer from multilayer adsorption of methanol on Fe(110) at 100 K. Adsorption of methanol at 300 K on Fe(110) leads to an Auger spectrum that we associate with an adsorbed methoxy species. The methoxy species was found to be stable to 350 K. These results are consistent with conclusions arising from high-resolution energy loss studies of the same system (*6*).

The Auger spectrum of a multilayer of methanol at 100 K is in agreement with a previous study (*2*), but the width of the peaks suggests that some electron beam-induced decomposition may have taken place. The electron doses used to record our spectra lie near the threshold for detectable damage to a thick methanol layer reported previously (*2*). We believe it unlikely that the spectra of chemisorbed methanol or methoxy species will have been affected by electron beam damage. These spectra were observed to change only after electron doses considerably larger than those necessary to record the spectra were used.

The dN_E spectrum of the adsorbed methoxy species (Fig. 3a) is quite distinctive and could therefore prove to be a useful fingerprint of this type of species, e.g., in situations where it may arise from reactions of adsorbed carbon monoxide and hydrogen. The twin negative deflections at 266 and 271 eV are assigned to the methyl group which is not bonded directly to the surface. It is interesting to compare this spectrum with that of the ethylidyne species ($CH_3—C\equiv$) adsorbed on Pt(111) which was reported earlier (*4*), as is done in Fig. 7. The N_E ethylidyne spectrum was found to contain a much more intense, broad high-energy peak attributable largely to the carbon atom attached directly to the metal surface, but the sharp features in the spectrum, accentuated in the differential

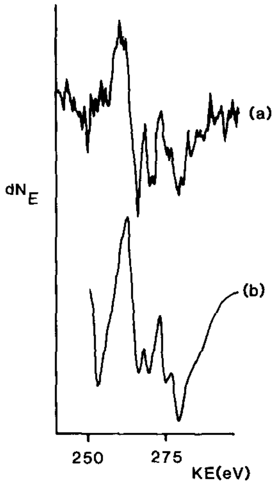

FIG. 7. (a) Carbon dN_E Auger spectrum of Fe(110) exposed to 0.5 L methanol at 300 K. (b) Carbon dN_E Auger spectrum of Pt(111) exposed to ethylene at 80 K and heated to 290–400 K (*4*).

mode, show a remarkable resemblance to the spectrum of the methoxy species. The obvious inference is that the distinctive dN_E spectra of Fig. 7 may be regarded as characteristic of surface species of the type $CH_3—X$, where X may be $O=$ or $C\equiv$, or presumably $CH=$ and $CH_2—$, i.e., where the methyl group is not bonded directly to the metal surface.

These results provide further evidence of the diagnostic power of Auger electron spectroscopy in studies of molecular adsorbates.

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