Electron spectroscopic studies of the adsorption and decomposition of methanol on transition metals. A review*

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Abstract. Results of investigations of the adsorption and decomposition of methanol on the surface of transition metals such as Fe, Ni, Cu, Pd, Ag, Mo, W and Pt by uv and x-ray photoelectron spectroscopy, electron energy loss spectroscopy, Auger electron spectroscopy and thermal desorption spectroscopy have been reviewed. The first step in the decomposition of CH_3OH on these metal surfaces is the formation of the methoxy species, OCH_3 radical. In the case of Fe, Mo and W, complete decomposition of CH_3OH occurs leaving $CO(\beta)$, H_2 and CH_4 on the surface. Dissociation proceeds upto $CO(\alpha)$ and H_2 on the surface of Ni, Pd and Pt whereas on Ag and Cu, selective oxidation of CH_3OH to H_2CO is preferred. The difference in the reactivity of metals towards CH_3OH is rationalised from the heats of adsorption of O_2, CO and H_2 on these metals.

Keywords. CH_3OH; adsorption; decomposition; x-ray photoelectron spectroscopy; uv photoelectron spectroscopy; electron energy loss spectroscopy; Auger electrons spectroscopy; thermal desorption spectroscopy.

1. Introduction

Interaction of alcohols with metal surfaces is an interesting reaction from the point of view of catalysis and corrosion. In corrosion, alcohols serve as models for water as they contain a reactive hydroxyl group. Metals such as copper and silver are used as highly specific catalysts for conversion of methanol to formaldehyde (Walker 1964). On Ni surfaces CH_3OH is, on the other hand, known to decompose to carbon monoxide (Kojima *et al* 1981). On Fe, methanol decomposes completely to carbon, oxygen, hydrogen and even methane formation has been noticed (Benziger and Madix 1980). In less reactive metals such as Ag, only when the surface is preadsorbed with oxygen methanol is known to be reactive giving rise to formaldehyde. Reaction of alcohols on metal surfaces serves as model for aqueous corrosion of metals.

With the advent of surface-sensitive techniques such as x-ray photoelectron spectroscopy (xps), uv photoelectron spectroscopy (ups), electron energy loss spectroscopy (eels), Auger electron spectroscopy (aes) and thermal desorption spectroscopy (tds), it is now possible to understand the nature of surface reactions by identifying the intermediate species formed on the surface. Selectivity of catalyst surfaces for specific reactions can be better understood in the light of such studies. While a large number of studies employing electron spectroscopy and related techniques are reported in the literature on the adsorption of molecules on metals, we have chosen methanol to demonstrate how complementary information can be obtained on its adsorption and

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dissociation on metals by different surface sensitive techniques. In this article, UPS, XPS, EELS, AES and TDS studies of the adsorption and decomposition of methanol on Fe, Ni, Cu, Pd, Ag, Mo, W and Pt surfaces have been reviewed.

2. UPS studies

A few UPS studies employing HeI (21·22 eV) or HeII (40·8 eV) radiation have been reported in the literature. CH_3OH is molecularly adsorbed on clean metal surfaces at low temperature (< 120 K). Changes in UPS on warming have been followed as a function of temperature. Typical spectra of CH_3OH on Cu surface are given in figure 1 (Yashonath *et al* 1982). In table 1, the electron states of chemisorbed CH_3OH on different metals are presented. HeI photoelectron spectra of gas phase CH_3OH (Turner *et al* 1970) show five distinct bands at 10·8, 12·7, 15·2, 15·6 and 17·7 eV. These bands are assigned to the ionization of electrons from $2a''(n_O)$, $7a'(n_O)$, $6a''(\sigma_{CO})$, $1a'(\pi_{CH_3})$ and $5a'(\pi'_{CH_3})$ molecular orbitals of CH_3OH (Turner *et al* 1970). The spectrum of molecularly chemisorbed CH_3OH on Cu given in figure 1 shows distinct peaks due to $2a''$, $7a'$, $(6a'' + 1a')$ and $5a'$ levels.

CH$_3$OH exposed to metals below 120 K gets either chemisorbed or condensed depending on the exposure. At these temperatures chemisorption is seen at exposures of 6–10L ($1L = 10^{-6}$ torr sec) while multilayer adsorption leading to condensation occurs at higher exposures. The CH_3OH orbitals are shifted to lower binding energies

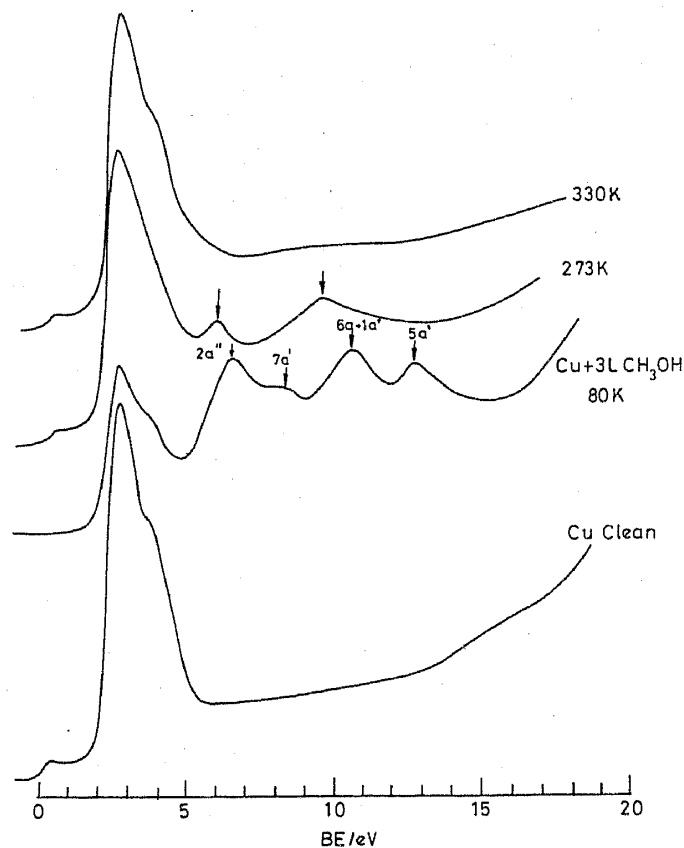**Figure 1.**   HeII UPS of Cu + CH_3OH as a function of temperature (Yashonath *et al* 1982).

Table 1. Electron states molecularly adsorbed CH_3OH on metals[a].

CH_3OH (gas phase)	10·8	12·7	15·2	15·6	17·7	(Turner *et al* 1970)
Fe + CH_3OH	6·1 (0·6)	7·6	10·1	—	12·4	(Yashonath *et al* 1982)
Ni + CH_3OH	5·8 (0·6)	7·0	9·8	—	12·3	(Yashonath *et al* 1982)
	5·2 (0·5)	7·2	9·6	—	12·0	(Rubloff and Demuth 1977)
	6·2 (0·3)	7·9 (0·6)	10·6	—	—	(Kojima *et al* 1981)
Cu + CH_3OH	5·8 (0·7)	7·2	9·6	—	12·0	(Bowker and Madix 1980)
	5·4 (0·9)	7·0 (0·4)	8·8	9·4	11·2	(Kojima *et al* 1981)
	6·5 (0·5)	8·1	10·6	—	12·8	(Yashonath *et al* 1982)
Pd + CH_3OH	4·9 (0·5)	6·2	8·8	—	11·0	(Luth *et al* 1977)
Pt + CH_3OH	4·9	6·3	8·9	—	11·2	(Sexton *et al* 1982)
Ag + CH_3OH	5·8	7·8	10·2	—	12·5	
$(Ag + K + O_2)$ + CH_3OH	5·7 (0·5)	7·5	10·0	—	12·5	

[a] All the binding energy values are given in eV; (0·6) is the chemical shift of this band due to chemisorption.

on adsorption when the reference level is taken from $E_F = 0$ instead of with reference to vacuum E_{BE} (vac). Luth *et al* (1977) have shown that all the electron states of condensed CH_3OH are shifted to lower binding energies by extra-atomic relaxation/polarisation effects in addition to the work function. In the condensed state, electron states of CH_3OH with reference to the vacuum level are given by:

$$E_{BE} \text{(vac)} = E_{BE} (E_F = 0) + \phi + \Delta\phi + E_R, \tag{1}$$

where ϕ is the work function of the metal and $\Delta\phi$ is the change in the work function due to adsorption of molecule. E_R is the extra-atomic relaxation/polarisation energy. The work function decreases by about 0·5 eV upon CH_3OH adsorption on metals such as Cu (Bowker and Madix 1980). Typically, E_R values vary from 1 to 2 eV. For instance E_R is 1·9 eV for Cu and 1·4 eV in the case of Pd (Luth *et al* 1977).

When the surface temperature is raised, first the condensed CH_3OH desorbs leaving behind the chemisorbed molecules on the surface. On Fe, Ni, Pd and Pt, chemisorption occurs below 120 K. Only in the case of Cu, chemisorption occurs even at 295 K at low coverages. CH_3OH is essentially physically adsorbed on clean silver at 120 K.

When CH_3OH is chemisorbed, energies of those molecular orbitals which form chemisorption bond with the metal are shifted to higher binding energies. In this case, $2a''$ orbital corresponding to $O(2p)$ lone pair lying parallel to the metal surface is shifted to higher binding energies by 0·4 to 0·9 eV as given in table 1. Studies by Kojima *et al* (1981) show shift of both $2a''$ and $7a'$ orbitals (both belonging to non-bonding $O(2p)$ orbitals of CH_3OH) in the case of Cu and Ni. Due to overlapping of $2a''$ and $Pt(5d)$ bands in the case of CH_3OH on Pt, shift in the $2a''$ orbital could not be seen (Sexton *et al* 1982). These observations reveal that charge transfer occurs from highest occupied molecular orbital $(2a'')$ of CH_3OH to the empty d bands of transition metals. Thus, when the CH_3OH is chemisorbed on the metal surfaces, bonding is essentially between the $O(2p)$ non-bonding orbitals and the metal d orbitals.

The reactivity of metal surfaces and the nature of intermediate species formed become clear from the studies at higher temperatures. Changes in the UPS spectra with temperature of CH_3OH adsorbed on metals are compared with the spectra of adsorbed H_2CO and CO recorded independently on the same metals. As has been mentioned earlier, H_2CO and CO are the prominent products of decomposition of CH_3OH on

metals. Carlson *et al* (1981) have studied adsorption of CH_3OH at 300 K and do not find molecular chemisorption at this temperature. Instead, they see peaks assignable to methoxy species. Bowker and Madix (1980) show that the four peaks seen at 140 K on Cu merge into two peaks at 5·2 and 8·9 eV. The spectra recorded by Bowker and Madix (1980) compare well with those observed by Carlson *et al* (1981) and Kojima *et al* (1981). That the peaks seen at 5·2 eV and 8·9 eV correspond to methoxy species on Cu is supported by a semi-empirical molecular orbital calculation (Carlson *et al* 1981). These peaks can be seen clearly on Cu at 273 K as shown in figure 1. Methoxy species — OCH_3(ad) is symmetric compared to CH_3OH on Cu and hence $2a''$ and $7a''$ as well as $6a'$ and $1a'$ bands merge and $5a'$ band shifts to lower binding energy. In principle, we should see three peaks due to $(2a'' + 7a')$, $5a'$ and $(6a' + 1a')$. However, the peak due to $5a'$ orbital seems to be of low intensity and therefore only two peaks at 5·2 and 8·9 eV are seen which are due to $(2a'' + 7a')$ and $(6a' + 1a')$ respectively. Formation of methoxy species on Cu has also been reported by Yashonath *et al* (1982) around 223 K.

On higher exposure of CH_3OH at 295 K (>600 L) on Cu surface, Kojima *et al* (1981) have noticed the formation of H_2CO. Peaks at 5·4, 8·4 and 10 eV which could be assigned to $2b_2$, $1b_1$ and $(1b_2 + 2a_1)$ orbitals of H_2CO are clearly seen. The peaks compare well with the ones due to the molecularly chemisorbed H_2CO on Cu at 295 K.

On Pt (Sexton *et al* 1982), Pd (Luth *et al* 1977), Ni (Rubloff and Demuth 1977; Kojima *et al* 1981; Yashonath *et al* 1982) and Fe (Yashonath *et al* 1982), CH_3OH is molecularly chemisorbed at temperatures below 120 K. On warming to 160–170 K, dissociation of methanol occurs to give CO(ad). In the case of Pt, CO formation from CH_3OH is clearly seen at 200 K; bands at 8·5 eV and 11 eV exactly match with those of CO adsorbed on Pt. The formation of methoxy species has been reported by Yashonath *et al* (1982) on Fe and Ni around 120 K; at 220 K, decomposition to CO occurs.

2.1   *UPS of CH_3OH on Cu and Ag precovered with oxygen*

Conversion of CH_3OH to formaldehyde is found to be enhanced on Ag surface precovered with oxygen (Wachs *et al* 1978). Bowker and Madix (1980) have shown that abstraction of hydrogen from methanol by alkaline oxygen on metal surfaces yields water and methoxy species. H_2O is liberated easily and the methoxy species decomposes to give H_2CO and H_2. UPS spectrum of CH_3OH on oxygen precovered Cu at 270 K clearly showed the formation of H_2CO.

The sticking probability of oxygen on clean silver is very low. One of the ways of activating the surface for enhanced adsorption of oxygen is to cover the surface with alkali metals (Ayyoob and Hegde 1983). On clean silver, CH_3OH is physically adsorbed and at 120 K, it gets desorbed completely leaving the surface clean. On potassium-covered silver surface (coverage less than 2×10^{14} atoms/cm²), adsorption of oxygen shows two distinct peaks at 4·5 eV and 8·5 eV as can be seen from the curve B of figure 2. When the surface was then exposed to CH_3OH at 100 K and on subsequent warming to 180 K, we see formation of H_2CO; the peaks at 5·5, 9·4 and 11·5 eV compare well with those of H_2CO(ad). On warming the surface to 300 K, the adsorbed species desorbs and O(2p) peak at 4·5 eV completely disappears. Only the 8·5 eV peak persists as can be seen from figure 2. Therefore, it is clear that only the lower binding energy O(2p) peak at 4·5 eV is active in the oxidation of CH_3OH.
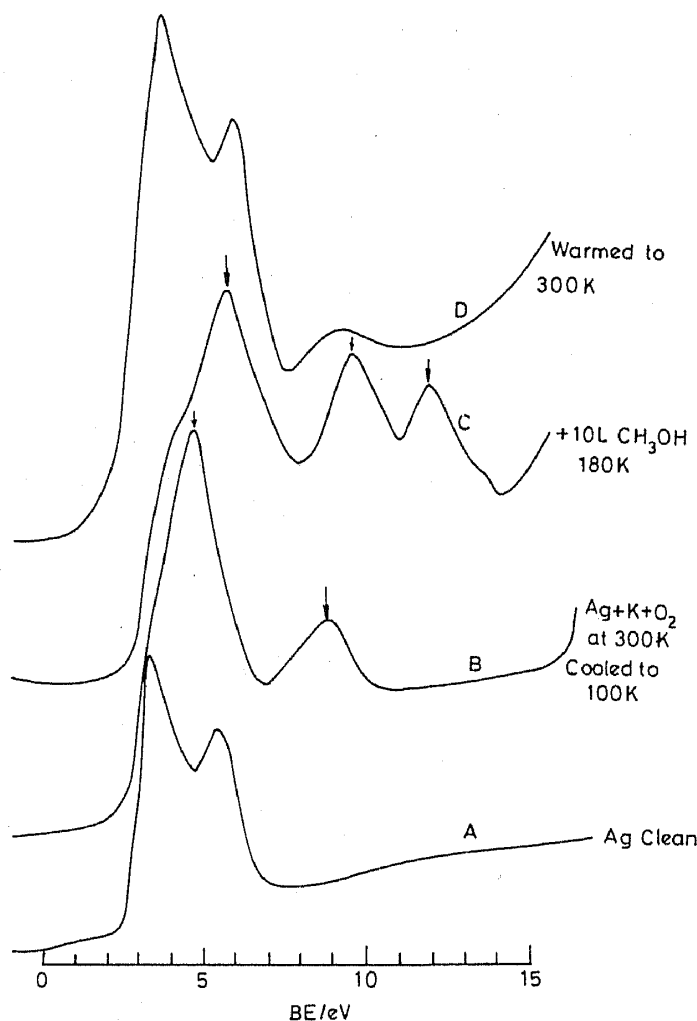
**Figure 2.** HeII UPS of $(Ag + K + O_2) + CH_3OH$ as a function of temperature.

3. XPS studies

In XPS studies, core level binding energies of molecules adsorbed on metals are monitored as a function of temperature. A few XPS studies of the adsorption of CH_3OH on metals as revealed through C(1s) and O(1s) are reported in the literature; Yashonath *et al* (1982) have reported changes in the C(1s) and O(1s) spectra of CH_3OH on Fe, Ni and Cu as a function of temperature. Benziger and Madix (1980) have studied dissociation of CH_3OH on Fe(100) and Sexton (1981) has reported similar studies on Pt(111) single crystals surfaces. XPS studies of CH_3OH on both clean and oxygen-covered Cu(110) have been carried out by Bowker and Madix (1980). We have studied recently adsorption of CH_3OH on potassium-covered Ag surface. O(1s) and C(1s) binding energies of adsorbed CH_3OH on various metals are summarised in table 2. Typical C(1s) and O(1s) spectra of CH_3OH adsorbed on Fe are shown in figure 3.

C(1s) binding energy of CH_3OH on metals below 140 K occurs at 286.2 ± 0.2 eV which is indicative of molecularly chemisorbed methanol. Simultaneous UPS studies in several of these cases support this observation. The O(1s) binding energy of CH_3OH on

Table 2. O(1s) and C(1s) core level binding energies of CH_3OH on metals.

System	Temp. (K)	O(1s)	C(1s)	Reference
$Fe(100) + CH_3OH$	200	532 eV	285·6 eV	Benziger and Madix (1980)
	350	531·2	285·4	
	500	530·1	282·2	
	900	530·1	282·2	
$Fe + CH_3OH$	80	533·0	286·2	Yashonath *et al* (1982)
	223	530·3	284·8	
	373	530·3	284·5	
$Ni + CH_3OH$	80	533·0	286·0	Yashonath *et al* (1982)
	300	530·6	284·0	
$Cu(110) + CH_3OH$	140	532·4	286·2	Bowker and Madix (1980)
	270	530·7	286·2	
$Cu(110) + O_2 + CH_3OH$	140	532·4	286·2	Bowker *et al* (1980)
	270	530·8	286·2	
$Pt(111) + O_2 + CH_3OH$	100	532·7	—	Sexton *et al* (1982)
	160	532·1	—	
	200	532·1	—	
$Ag + CH_3OH$	100	533·3	286·6	
$Ag + K + O_2$	300	528·6	—	Ayyoob and Hegde (1983)
		530·5		
$Ag + K + O_2 + CH_3OH$	100	533·3	286·7	
	120	530·7	286·2	
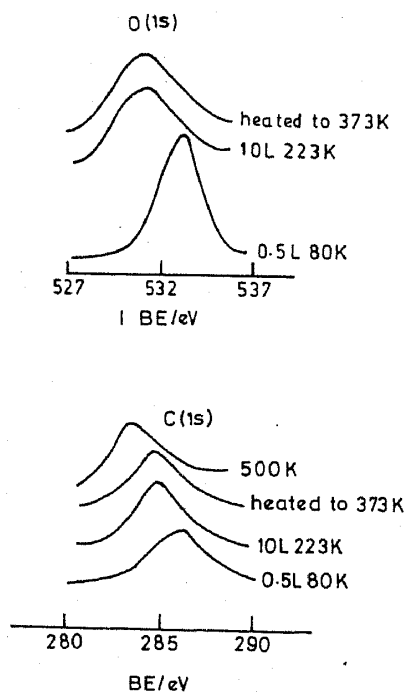
Figure 3. C(1s) and O(1s) xps of CH_3OH on Fe as a function of temperature (Yashonath *et al* 1982).

metals generally occurs at $532 \cdot 4 \pm 0 \cdot 4$ eV. On raising the temperature of CH_3OH adsorbed on Fe and Ni from 140 to 300 K, the O(1s) peak shifts from $532 \cdot 4$ to $530 \cdot 3$ $\pm 0 \cdot 2$ eV and C(1s) from $286 \cdot 2$ to $284 \cdot 5$ eV. This is attributed to the formation of CO by the dissociation of CH_3OH. On further heating, only on Fe, dissociation of CO occurs with the formation of elemental carbon the C(1s) binding energy being at $282 \cdot 2$ eV. On Pt, even at 200 K, dissociation of CH_3OH to CO is seen and O(1s) binding energy at $532 \cdot 1$ eV compares well with that of CO adsorbed on Pt. On Cu, however, molecularly chemisorbed CH_3OH is found to decompose to H_2CO as indicated by the O(1s) peak at $530 \cdot 7$ eV; the C(1s) remains at $286 \cdot 2$ eV. On heating to 350 K, O(1s) and C(1s) peaks disappear indicating the desorption of H_2CO.

On clean silver, CH_3OH condenses at 100 K. The C(1s) peak at $286 \cdot 2$ eV and O(1s) at $533 \cdot 3$ eV disappear as soon as the temperature is raised to 120 K. However, when Ag surface is precovered with potassium and oxygen, and subsequently exposed to CH_3OH at 140 K, the decomposition of CH_3OH occurs to give H_2CO which desorbs at higher temperatures. Further decomposition to give CO or CO_2 does not seem to occur as indicated by C(1s) binding energies (table 2).

The results show that xps is a valuable technique for the study of adsorption and reactions of organic molecules such as CH_3OH on metal surfaces. The core levels C(1s) and O(1s) clearly reveal the nature of surface species formed. For instance, C(1s) value around $286 \cdot 2$ eV is characteristic of methoxy species.

4. EELS studies

High resolution eels is one of the recent electron spectroscopic techniques. Here, a highly monochromatic electron beam of low kinetic energy ($3 \cdot 5$ eV; fwhm $= 8$–10 meV or 60–80 cm^{-1}) impinges on the solid surface. The specularly-reflected electron beam is energy analysed. The vibrational modes of adsorbed molecules are excited by the electron beam and correspondingly, energy loss peaks in the lower kinetic energy region are observed. Loss in energy measured is equal to the vibrational excitation energy. Further details of this technique are given by Rao *et al* (1981).

On clean Cu, no adsorption of CH_3OH occurs. However, on Cu preadsorbed with oxygen, CH_3OH shows the formation of OCH_3 species with all the characteristic vibrational frequencies in the eels (figure 4 and table 3). Ni and Pt show a different behaviour. At 100 K CH_3OH is first chemisorbed on both the metals, as revealed by a lowering of OH stretching frequency from 3670 cm^{-1} (gas phase value) to 3215 cm^{-1} as well as the presence of a metal-oxygen frequency at 600–700 cm^{-1}. At higher temperatures (150 K), OCH_3 species is seen which subsequently converts to CO. Characteristic M–C–O modes are clearly identifiable in the eels (table 3). Pt–H is also noticed at this temperature. On Fe, only OCH_3 species is seen even upto 300 K. This observation is contrary to what is observed in the ups and xps study of CH_3OH on iron where formation of CO is seen around this temperature. On palladium, CH_3OH is chemisorbed at 140 K in the eels study, but no studies at higher temperatures have been reported. The results indicate that the eels is a valuable complimentary technique for the investigation of surface species on metals.
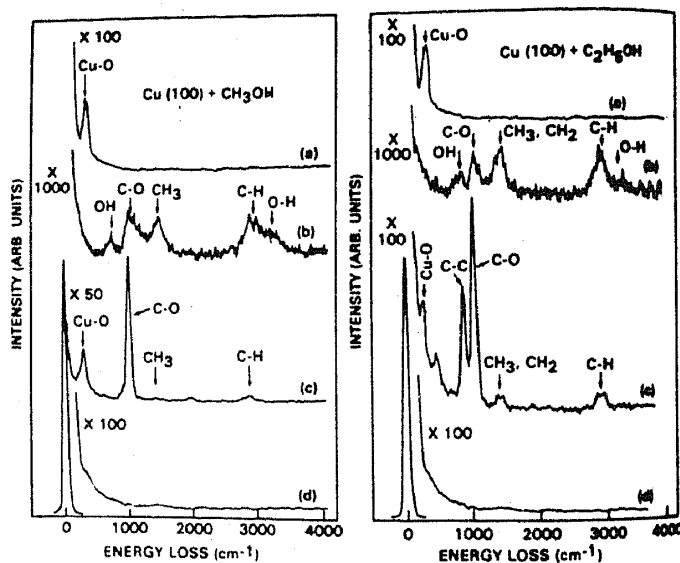
Figure 4. Typical electron energy loss spectra of methanol with pre-adsorbed oxygen on Cu(100) (after Sexton 1979).

5. AES studies

AES has been primarily used to characterise the elements at the solid surfaces. Rao *et al* (1980) have shown that AES can be used to study the oxidation states of transition metals by Auger intensity ratio technique. In this method, 3 to 5 keV electron beam impinges on the metal surface. KLL, LMM or MNN Auger electrons (depending on the metal under consideration) are energy-analysed. When a molecule such as CH_3OH is adsorbed on the surface, additional peaks due to $O(KLL)$ and $C(KLL)$ in the Auger spectra are seen which give information on the nature of adsorption and dissociation.

Auger electron spectroscopy is useful to study the adsorption phenomena. Electron beam initiated Auger spectra show characteristic 'finger print' features for the various adsorbed species. This technique has been used for the investigation of CO adsorption on transition metals (Hooker and Grant 1977; Kamath *et al* 1982b).

Kamath *et al* (1982b) have applied this technique to study the interaction of CH_3OH with oxygen precovered Cu. The Auger spectra in the $O(KLL)$ region of a related series of molecules CH_3OH, CH_3COCH_3 and CH_3COOCH_3 are shown in figure 5. It is evident that the high kinetic energy peak around 523 eV is characteristic of methoxy oxygen, while the peaks at 516 and 511 eV are characteristic of carbonyl oxygen (see spectrum of CH_3COCH_3, CH_3COOCH_3), which contains both the methoxy and the carbonyl oxygen. Auger spectra of CH_3COOCH_3 show a composite spectrum containing features due to both methanol and acetone.

The Auger spectrum in the $O(KLL)$ region of CH_3OH on Cu shows interesting changes on warming. At 173 K, the high kinetic energy feature attributed to the methoxy oxygen disappears and peaks at 512·5 and 507 eV are seen with a line shape very similar to that of CH_3COCH_3, but uniformly shifted to lower kinetic energy by about 3 eV. This can be assigned to the carbonyl species, probably H_2CO, obtained from CH_3OH oxidation. Similar observations have been made by Yashonath *et al* (1982) and Kojima *et al* (1981) from UPS and XPS studies.

Table 3. Vibrational frequencies (cm^{-1}) of adsorbed methanol and intermediates on metals from EELS studies.

System	Surface species	$\nu_{(M-O)}$	$\nu_{(M-H)}$	$\nu_{(M-C)}$	$\nu_{(C-O)}$	$\nu_{(CH_3)}$	$\nu_{(C-H)}$	$\nu_{(C-H)}$	$\nu_{(O-H)}$	References
CH_3OH molecule	CH_3OH	—	—	—	1030	1430	2840	2940	3670	Rao (1963)
Cu(110)+O_2	Cu-O	330	—	—	—	—	—	—	—	Sexton (1979)
Cu(110)+O_2+CH_3OH at 370 K,		290	—	—	—	—	—	—	—	
Cooled to 100 K	Cu-OCH_3	290	—	—	1010	1450	2830	2910	—	-do-
Ni(111)+CH_3OH at 140 K	CH_3-O-H	685	—	—	1035	1456	2800	2950	3215	Demuth and Ibach (1979)
at 180 K	Ni-OCH_3	500	—	—	1040	1440	2800	2955	—	-do-
at 300 K	Ni-CO	—	—	390	1850	—	—	—	—	-do-
Pt(111)+CH_3OH 100 K	CH_3OH condensed	680	—	—	970	1410	—	2930	3200	Sexton (1981)
155 K	CH_3OH	700	—	—	1000	1430	—	2930	3280	-do-
	Chemisorbed	680	—	—	1060	—	—	—	—	-do-
300 K	Pt-OCH_3 / Pt-CO, Pt-H	—	1210	470	2080	—	2910	2950	—	-do-
400 K	Pt-CO	—	—	470	2080	—	—	—	—	-do-
Pt+(111)+O_2+CH_3OH, 170 K	Pt-OCH_3	370	1200	—	1430	—	—	2910	—	
300 K	Pt-CO, Pt-H	—	1230	470	2080	—	—	2930	—	
Fe(110)+CH_3OH 120 K	Fe-OCH_3	380	—	—	1020	1450	2840	—	—	McGreen et al (1983)
heated to 300 K	Fe-OCH_3	380	—	—	1050	1435	2830	—	—	-do-
cooled to 120 K		—	—	—	—	—	—	—	—	
Pd(100) 140 K	Pd-OCH_3	685	—	—	1025	1455	2845	2945	3345	Christmann and Demuth (1982)
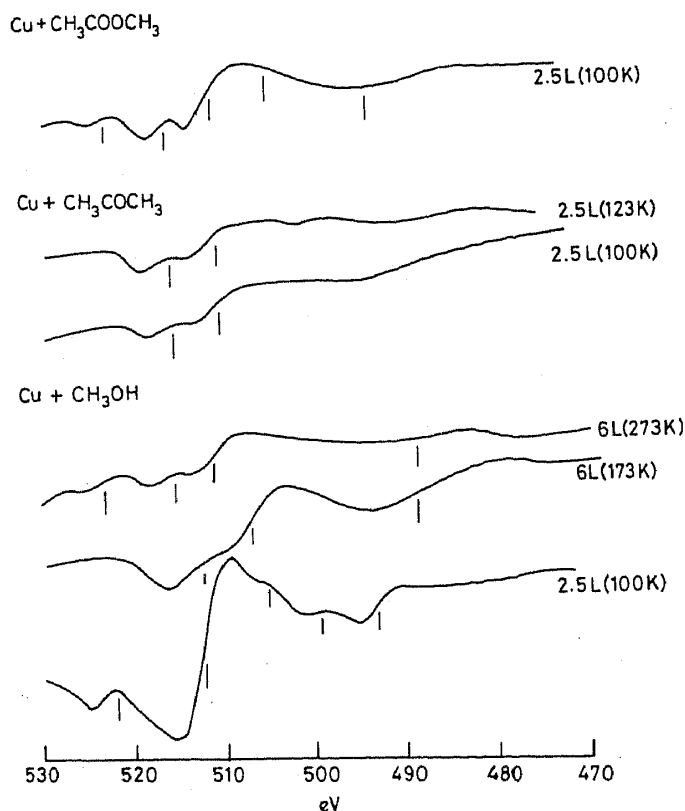
Figure 5. O(KLL) Auger spectra of CH_3OH, CH_3COCH_3 and CH_3COOCH_3 on Cu (after Kamath *et al* 1982).

It would be interesting to study the adsorption of CH_3OH on metals such as Ni, Pd and Pt by AES to follow the dissociation of CH_3OH to CO(ad).

6. Thermal desorption studies

While XPS, UPS, EELS and AES studies give information on the molecules in the adsorbed state, thermal desorption technique provides information on the nature of species leaving the surface on flash desorption. In this method, clean metal is dosed with reactant molecules. The surface is heated at a linear rate of 20–30° per sec. The atoms, molecules or ions leaving the surface are mass-analysed using a quadrupole mass spectrometer. A plot of the intensity of a particular mass peak *vs* temperature is generally referred to as the thermal desorption spectrum. When methanol adsorbed on clean or oxygen precovered metal is flash-desorbed, mass peaks of the undissociated CH_3OH and several decomposition products are seen in the TDS. TDS also provide additional information on the heats of desorption. The rate of desorption per unit surface area can be written as:

$$N = \gamma_n \sigma^n \exp\left(-E/RT\right),$$

where N is the number of molecules leaving the surface per unit area, n is the order of desorption, σ is the surface coverage (molecules/cm^2) and γ_n is the frequency factor. E is the activation energy of desorption (cals/mol). A plot of $\ln(N)$ *vs* $1/T$ gives the

Table 4. Desorption temperature of molecules from CH_3OH decomposition on metals.

Molecule/metal	Ag(111) (Wachs et al 1978a)	Cu(110) (Wachs et al 1978b)	Ni (Steinbach and Spengler 1981)	Pd(100) (Christmann and Demuth 1982)	Fe(100) (Benziger and Madix 1980)	Mo(100) (Ko and Madix 1981)	W(100) (Ko et al 1980)
$HCOOCH_3$	250–280 K	—	—	—	—	—	—
$CH_3OH(\alpha)$	280	200–275 K	110–320 K	—	270 K	250 K	250 K
$CH_3OH(\beta)$	300	365–390	—	160–200	450	350	500
H_2CO	250–400	365–390	210	—	—	350	—
H_2	400	325–470	450–500	325	350	275–400	300–600
$CO(\alpha)$	—	—	450–550	475	450	335	500
$CO(\beta)$	—	—	—	—	800	1500	1500
CO_2	400	470	—	—	—	—	—
H_2O	250–280	238–470	—	—	—	—	—
CH_4	—	—	—	—	450	500	500
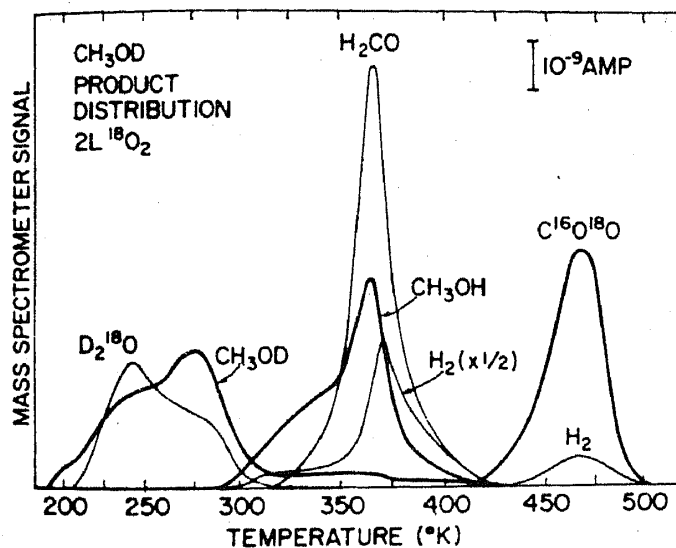
Figure 6. Typical thermal desorption spectra of CH_3OH on $Cu(110)$ (after Wachs and Madix 1978b).

activation energy of desorption directly. In most cases, adsorption of molecules is non-activated and therefore, the activation energy E is approximately equal to the heat of adsorption. Further details on the TDS technique are given in the review by King (1975).

Thermal desorption study of CH_3OH has been carried out on Ag, Cu, Ni, Pd, Fe, Mo and W. Products desorbing from the surface along with desorption temperature on these metals have been summarised in table 4. Typical thermal desorption spectrum is shown in figure 6.

TDS results showing the fragments leaving the metal surface (see table 4) agree well with what is observed by other techniques. CH_3OH desorption from Ag and Cu surfaces precovered with oxygen is quite similar in nature. Both the metals give a high yield of H_2CO. Simultaneous desorption of CO_2 and H_2 from these metal surfaces has been attributed to the presence of a surface formate species obtained from the oxidation of H_2CO. In addition, desorption of $HCOOCH_3$ is seen in the case of Ag.
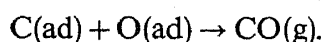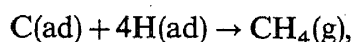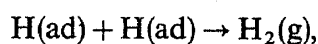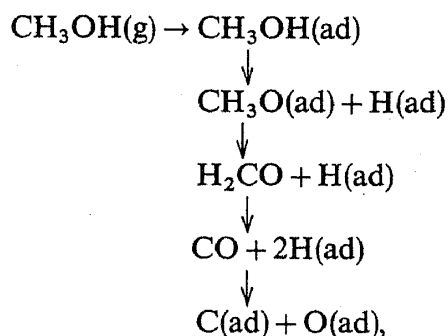
CO and H_2 are the main desorption products from CH_3OH on Ni and Pd. Desorption of molecular $CO(\alpha)$ from Ni and Pd surfaces takes place around 450 to 500 K. It is clear, therefore, that CH_3OH decomposes on these metals into CO and H_2 as is clearly seen by UPS, XPS and EELS studies.

On Fe, Mo and W, one of the desorption products is CH_4. Also, desorption of $CO(\beta)$ at temperatures well over 1000–1500 K is seen. This arises from the surface carbide and oxide species. Thus, on these metals, complete dissociation of CH_3OH into C, O and H occurs. This observation is supported by XPS study on Fe as discussed earlier (§§2 and 3). TDS is therefore a valuable addition to the electron spectroscopic techniques for the characterization of surface species.

7. Reactivity of CH_3OH on metal surfaces

From the survey of interaction of CH_3OH on various metals, we can classify the metals into three categories.

(a) The first category consists of Fe, Mo, W and others further left in the periodic table. These metals have very high heats of formation of their respective oxides and carbides. Although the first step in the decomposition of CH_3OH on these metals is the formation of methoxy species, as seen by UPS and EELS studies on Fe for example, the methoxy species dissociates completely into $C + H + O$. The $CO(\beta)$ desorbs from these metals at temperatures varying between 800 K (Fe) and 1500 K (W and Mo). The reaction of CH_3OH on these metals can be summarised as below:

$$CH_3OH(g) \rightarrow CH_3OH(ad)$$
$$\downarrow$$
$$CH_3O(ad) + H(ad)$$
$$\downarrow$$
$$H_2CO + H(ad)$$
$$\downarrow$$
$$CO + 2H(ad)$$
$$\downarrow$$
$$C(ad) + O(ad),$$

$$H(ad) + H(ad) \rightarrow H_2(g),$$
$$C(ad) + 4H(ad) \rightarrow CH_4(g),$$
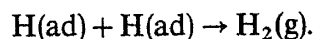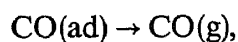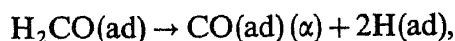$$C(ad) + O(ad) \rightarrow CO(g).$$

This reaction behaviour can be understood in terms of the heats of adsorption of molecular *vs* dissociative adsorption of CO on these metals (table 5). From the data it is seen that dissociative adsorption of CO on these metals is preferred to molecular adsorption.

(b) The second category of metals Ni, Pd and Pt show the formation of the $CO(\alpha)$ species from CH_3OH. Heats of molecular CO adsorption on these metals is more negative than the values for dissociative chemisorption (see table 5). Also, heat of oxygen adsorption is not too high. Consequently, CH_3OH decomposition does not go beyond the formation of $CO(\alpha)$ species. Therefore, the reaction of CH_3OH on these metals may be formulated as:

$$CH_3OH(g) \rightarrow CH_3OH(ad) \rightarrow CH_3O(ad) + H(ad),$$
$$CH_3O(ad) \rightarrow H_2CO(ad) + H(ad),$$
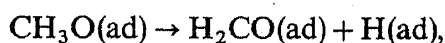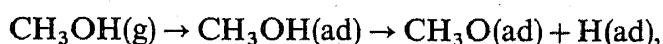
Table 5. Heats of adsorption of H_2, CO and O_2 on metals (in KJ/mol) (Kamath *et al* (1982a)).

Metal	H_2 (dissociative)	CO (Molecular)	CO (Dissociative)	O_2 (Dissociative)
Ag	−25	−27	+334	−62
Cu	−50	−71	+21	−326
Fe	−86	−105	−136	−546
W	−70	−88	−215	−570
Mo	−75	−90	−185	−544
Ni	−90	−109	−88	−488
Pd	−101	−142	+25	−170
Pt	−71	−127	+110	−133

$$H_2CO(ad) \rightarrow CO(ad)\,(\alpha) + 2H(ad),$$

$$CO(ad) \rightarrow CO(g),$$

$$H(ad) + H(ad) \rightarrow H_2(g).$$

(c) The third category consists of Cu and Ag which do not seem to adsorb CO. However, molecular CO is seen on Cu (Jagannathan *et al* 1980) at low temperature. Clean Ag and Cu merely show molecular adsorption and desorption of CH_3OH. However, on oxygen precovered surfaces, methoxy species is stabilized *via* hydrogen abstraction reaction:

$$2CH_3OH(ad) + O(ad) \rightarrow 2CH_3O(ad) + H_2O(ad),$$

$$H_2O(ad) \xrightarrow{150\ K} H_2O(g).$$
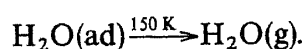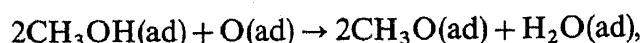
Methoxy species is stable even upto 370 K on Cu and no $CO(\alpha)$ is seen in any of the experiments reported. Further reaction of methoxy species is shown below:

$$CH_3O(ad) \rightarrow H_2CO(ad) + H(ad),$$

$$H_2CO(ad) \rightarrow H_2CO(g)$$
$$\quad\quad\quad\;\; \left|\xrightarrow{O(ad)} H_2COO(ad),\right.$$

$$H_2COO(ad) \rightarrow HCOO(ad) + H(ad),$$

$$HCOO(ad) \rightarrow CO_2(g) + H(ad),$$

$$H(ad) + H(ad) \rightarrow H_2(g).$$
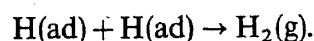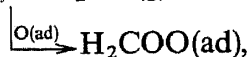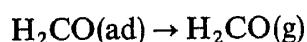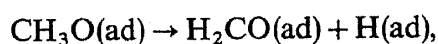
TDS studies on Cu and Ag provide support to the above scheme.

In the case of Ag, additional reactions

$$H_2CO(ad) + CH_3O(ad) \rightarrow H_2COOCH_3(ad),$$

$$H_2COOCH_3(ad) \rightarrow H(ad) + HCOOCH_3(g),$$
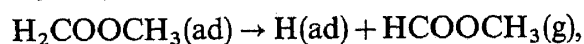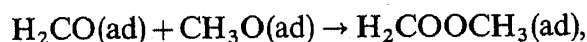
have been found to occur. $HCOOCH_3$ has been isolated in the TDS studies.

The classification of metals studied into three categories, reveals that metals to the left of the periodic table tend to stabilise elemental species (C, H and O), while those to the right tend to stabilise larger molecular species on the surface. While this observation is interesting in itself, it would be worthwhile if the surface can be modified to stabilise large molecular species on metals such as Mo and W. One attempt in this direction was to see the reactivity of partially oxidised or carburised W and Mo surface by Ko *et al* (1980). On W precovered with oxygen or C, the surface was passivated and on such a surface, CH_3OH was just chemisorbed and desorbed, a behaviour identical to clean Ag or Cu.

The present survey has shown that no study of CH_3OH on alloy surfaces has been made. It would be interesting to study the reactivity of CH_3OH on alloy surfaces such as Cu–Mn, Cu–Pd, Cu–Au, Ni–Fe where it would be possible to change the dissociation pathways compared to the clean metals.

the adsorption of methanol and for valuable comments and to Dr J Gopalakrishnan for helpful discussion.

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