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ADSORPTION OF METHANOL ON THE SURFACES OF COPPER ALLOYS. UPS AND EELS STUDIES[+]

Kuniyil PRABHAKARAN, Manjanath Subraya HEGDE,
and
Chintamani Nagesa Ramachandra RAO*
Solid State and Structural Chemistry Unit,
Indian Institute of Science,
Bangalore 560 012, India

Methanol adsorbs molecularly on the surfaces of Cu-Pd alloys at low temperatures and transforms to CH_3O or CO on warming, depending upon the alloy composition. On oxygen presorbed Cu-Pd alloy surfaces, adsorption of methanol gives rise to H_2O and H_2CO. CH_3OH adsorbed molecularly on the surfaces of Cu-Au alloys and CH_3O is formed only at relatively high temperatures.

Adsorption of CH_3OH on transition metal surfaces has been investigated by several workers by employing electron spectroscopic techniques. For example, it is known that CH_3OH transforms to CH_3O radical on a clean copper surface[1,2] and to H_2CO on a copper surface containing presorbed oxygen atoms.[3] On Pd and Ni surfaces, dissociation of CH_3OH to CO and H_2 has been reported.[4,5] In this laboratory, we have been carrying out comparative studies of the behaviour of metallic alloys and their component metal surfaces with respect to molecular adsorption and subsequent transformation of the molecules. Thus a recent study of the adsorption of carbon monoxide on the surfaces of copper alloys has shown the presence of a multiplicity of surface sites.[6] In this communication, we report the results of our studies on the adsorption of CH_3OH on clean as well as oxygen-covered Cu-Pd and Cu-Au alloy surfaces by employing ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS).

The UPS and XPS measurements were carried out with a ESCA-3 Mark 2 spectrometer of V.G. Scientific Ltd. EELS measurements were carried out simultaneously with XPS by employing ESCA-5 spectrometer of the same company. The alloys were prepared by melting the pure components in an induction furnace in an Ar atmosphere ; the resulting alloys were annealed in vacuum (at 900K) and rolled into 0.5 mm thick foils. The surface composition of the freshly cleaned surfaces of the alloys were determined following the method of Powell and Larson [7] by

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taking intensity ratios of Pd($3d_{5/2}$) and Cu($2P_{3/2}$) peaks in the case of Cu-Pd alloys and of Cu($3P_{3/2}$, $3P_{1/2}$) and Au($4f_{7/2}$) peaks in the case of Cu-Au alloys. The surface compositions were close to that of the bulk at 300 K. Adsorption of CH_3OH was carried out by exposing the alloy surfaces to the vapour at 80K in small doses (5-10 L ; 1 L = 10^{-6} Torr.s). In order to study the effect of presorbed oxygen the surface was first exposed to oxygen (50 L) at 300 K and the surface then cooled to 80 K. The presence of atomic oxygen was confirmed by monitoring O(1s) region (530 eV peak) in the XPS.

On clean $Cu_{0.91}$ $Pd_{0.09}$, CH_3OH is adsorbed molecularly at 80 K as evidenced by the following vibrational frequencies in EELS (Fig. 1) : 3258 cm^{-1} (ν OH), 2968 cm^{-1} (ν CH) 1484 cm^{-1} (δCH_3), 1048 cm^{-1} (ν CO) and 775 cm^{-1} (OH libration). In the UPS (Fig. 2) characteristic peaks of CH_3OH at 6.2 eV (2a" n_O), 7.9 eV (7a' n_O), 10.8 eV (6a" [σ CO+1a'CH_3]) and at 12.7 eV (5a' CH_3) are seen. On warming the surface to 170 K or above, CH_3OH transforms to CH_3O species as characterized by the disappearance of OH stretching band and the band due to OH libration in EELS (Fig. 1). The first overtone of the C-O stretching vibration (2120 cm^{-1}) also becomes prominent. The formation of CH_3O is evidenced in the UPS by the appearance of only two peaks at 5.5 eV (2a" n_O + 7a' n_O) and at 9.2 eV (6a' + 1a" + 5a') as seen in Fig. 2. The CH_3O species continues to remain on the surface upto 300 K. The formation of CH_3O from CH_3OH on $Cu_{0.91}$ $Pd_{0.09}$ surfaces is akin to that found on Cu(110) or polycrystalline surfaces.[2,3]

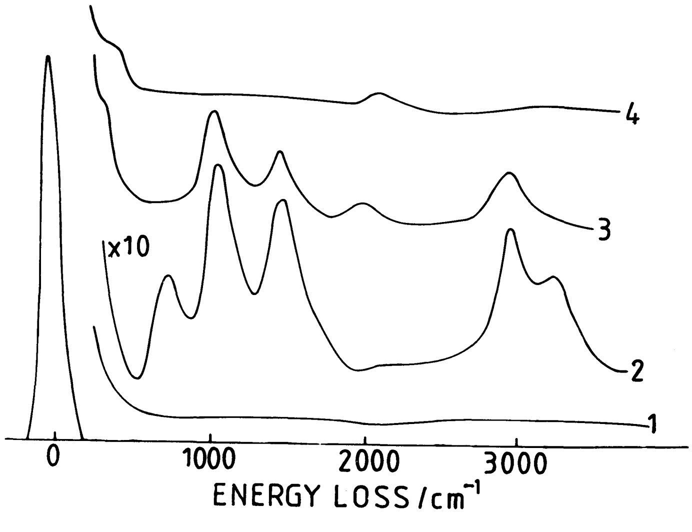

Fig. 1. EEL spectra.
1: Clean $Cu_{0.91}Pd_{0.09}$;
2: CH_3OH(10 L) adsorbed on $Cu_{0.91}Pd_{0.09}$ surface at 80 K;
3: 2 warmed to 170 K;
4: CH_3OH (10 L) adsorbed on $Cu_{0.75}Pd_{0.25}$ at 80 K and then warmed to 220 K

On a clean surface of $Cu_{0.75}Pd_{0.25}$ CH_3OH is molecularly adsorbed at 80 K. On warming to 220 K, we see evidence for the formation of carbon monoxide as shown by the characteristic stretching frequency at 2130 cm^{-1} and a metal-carbon stretching frequency at 450 cm^{-1} (Fig. 1); characteristic bands of CO are seen in

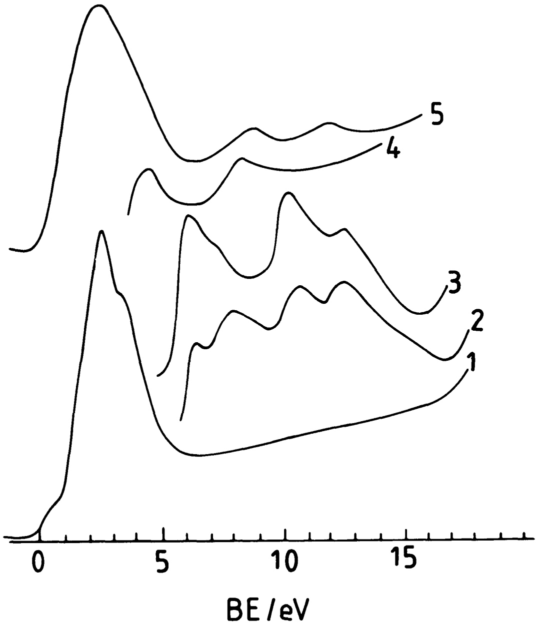

Fig. 2. HeII UPS spectra.
1: Clean $Cu_{0.91}Pd_{0.09}$ surface;
2: CH_3OH (10 L) adsorbed on $Cu_{0.91}Pd_{0.09}$ at 80 K;
3: 2 warmed to 120 K;
4: 3 warmed to 170 K 5: CH_3OH (10 L) adsorbed on $Cu_{0.75}Pd_{0.25}$ at 80 K and then warmed to 220 K

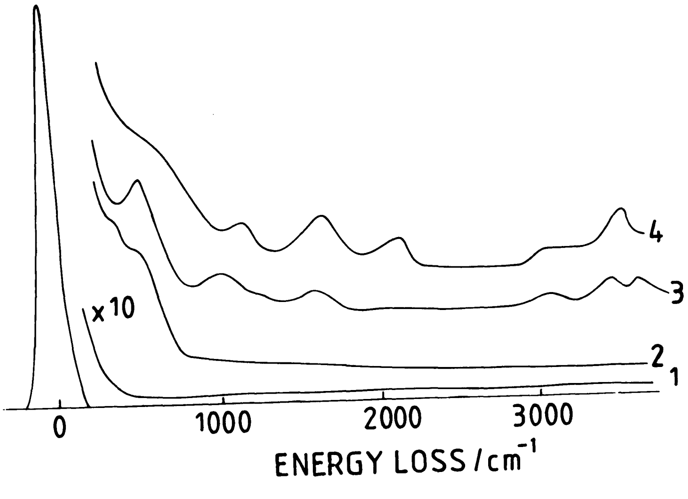

Fig. 3. EEL spectra.
Clean $Cu_{0.91}Pd_{0.09}$; 2: Oxygen (50 L) adsorbed on $Cu_{0.91}Pd_{0.09}$ at 300 K and then cooled to 80 K;
3: CH_3OH (6 L) adsorbed at 80 K on $Cu_{0.91}Pd_{0.09}$ surface containing presorbed atomic oxygen (as in 2);
4: CH_3OH (20 L) adsorbed on $Cu_{0.75}Pd_{0.25}$ surface containing presorbed atomic oxygen.

UPS as well (Fig. 2). This mode of decomposition of CH_3OH on $Cu_{0.75}Pd_{0.25}$ surface is similar to that found on Pd surface.$^{5)}$

On the surface of $Cu_{0.91}Pd_{0.09}$ containing presorbed atomic oxygen (50 L O_2 at 300 K), adsorption of CH_3OH at 80 K gives rise to two OH stretching frequencies at 3520 cm^{-1} and 3650 cm^{-1}. In addition there are peaks at 3040 cm^{-1}, 1670 cm^{-1} and 1078 cm^{-1} (Fig. 3). The 1670 cm^{-1} peak is likely to be due to the scissoring mode of H_2O rather than due to C = O stretching of H_2CO, the water being produced by the hydroxyl proton abstraction (from CH_3OH) by the adsorbed oxygen atoms on the surface. Such proton abstraction from adsorbed water has been reported in the literature.[8)] The two OH stretching frequencies are probably due to CH_3OH and H_2O-M. The reactions on the surface are suggested to be :

$$2CH_3OH(ads) + O(ads) \rightarrow 2CH_3O(ads) + H_2O(ads) \quad (1)$$
$$2CH_3OH(ads) + O(ads) \rightarrow 2H_2CO(ads) + H_2O(ads) + H_2 \quad (2)$$

Of the above two reactions, (1) is probably predominant in the case of $Cu_{0.91}Pd_{0.09}$. On the $Cu_{0.75}Pd_{0.25}$ surface covered with oxygen atoms, however we clearly see evidence for the formation of H_2CO with the characteristic carbonyl stretching frequency at 1720 cm^{-1} and a band at 1235 cm^{-1} due to CH_2 wag (Fig. 3). We also see OH stretching peak due to the H_2O-M species. The preponderant reaction on this surface is likely to be (2). The peak at 2170 cm^{-1} could be due to CO formed by the decomposition of H_2CO or CH_3OH.

On $Cu_{0.95}Au_{0.05}$ and $Cu_{0.89}Au_{0.11}$ surfaces both UPS and EELS shows that CH_3OH is both physisorbed and chemisorbed at 80 K, the latter continues to remain on the surface above 100 K. CH_3O seems to be formed only at relatively high temperatures. Since we observe a OH stretching frequency of 3500 cm^{-1} in the 100 - 300 K range, on the oxygen covered Cu-Au surfaces proton abstraction from CH_3OH seems to occur to some extent on these surfaces as well.

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