Intermolecular migration of methyl groups at a Cu(211) surface

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The exposure of preadsorbed oxygen to monomethylamine or the coadsorption of a 2 : 1 monomethylamine (CH_3NH_2)/dioxygen mixture at a Cu(211) surface at room temperature results in the formation of a surface species characterised by C(1s) and N(1s) binding energies of 285.2 and 398.2 eV, respectively, with a calculated carbon to nitrogen ratio of 2 : 1. This species, which we assign to a chemisorbed dimethylamine ($(CH_3)_2NH_x(a)$), is the only adsorbed product of the reaction and its formation must involve the breaking of a carbon–nitrogen bond and the intermolecular transfer of a methyl group.

Keywords: surface, chemisorption, methylamine, oxygen, methyl, XPS, copper, migration

1. Introduction

We report surface spectroscopic evidence for the activation of carbon–nitrogen bonds at a Cu(211) surface at room temperature and the intermolecular transfer of a methyl group between adsorbed amine molecules. This process maybe of interest to the catalytic community in respect of chain building reactions such as Fischer–Tropsch. The system we have studied is the chemisorption of monomethylamine (CH_3NH_2) in the presence of oxygen. Our objective was to investigate the properties of the molecule at oxidised surfaces with the aim of comparing its behaviour to that of ammonia – which has been studied in detail by this group [1–3] and by others [4–6] and with its oxygen analogue, methanol, which has also been extensively studied at copper surfaces [7–11]. Previous studies of monomethylamine [12–17] have considered almost exclusively its interactions with clean metal surfaces and utilised in the main temperature-programmed desorption (TPD) and vibrational spectroscopy (RAIRS). Whilst these methods give some information about the nature of the species on the surface, neither is easy to quantify. In contrast, the present work utilises X-ray photoelectron spectroscopy (XPS) which has a well established track record for providing accurate surface concentration data [18]. In the case of methylamine reacting with oxygen at copper surfaces, quantification of the data turns out to be of crucial significance.

2. Experimental

The XPS spectra were recorded on a Vacuum Generators photoelectron spectrometer equipped with an Al Kα photon source. All O(1s), C(1s) and N(1s) spectra were recorded with a pass energy of 50 eV and the binding energy scale calibrated to the Cu($2p_{3/2}$) peak at 932.7 eV. Cooling is achieved using liquid nitrogen flowing through a reservoir close to the sample and heating, with a heating element in the probe. Maximum heating rates were approximately 5 K per minute. The temperature of the sample was measured using a thermocouple mounted close to the sample holder. The purity of the dioxygen (Argo Ltd., 99.99%) and methylamine (Argo Ltd., 99.0%) gases was checked with an *in situ* quadrupole mass spectrometer and in the case of the latter confirmed by condensing it onto the sample at 80 K. This gave rise to single peaks in the N(1s) and C(1s) regions only, with a C : N ratio of 1 : 1. XPS data were acquired using commercial software (Spectra, R. Unwin) and analysed using software developed in-house. Surface atom concentrations and atom ratios were obtained using quantification procedures which have been described in detail elsewhere [18].

3. Results

3.1. Monomethylamine adsorption at clean Cu(211) surfaces

Monomethylamine does not adsorb at Cu(211) surfaces at room temperature but physisorbs at lower temperatures. Figure 1 shows C(1s) and N(1s) spectra recorded after about a monolayer of monomethylamine was adsorbed at 80 K. In the C(1s) region the dominant peak occurs at 286.8 eV similar to that observed for the methyl group of a chemisorbed methoxy species. The N(1s) peak, on the other hand, lies at 400.4 eV close to the binding energy observed for adsorbed ammonia. Taking into account the larger photoelectron cross section of the nitrogen, the C : N ratio at the surface is calculated to be 1 : 1. Whilst XPS cannot provide direct evidence for the activation of N–H bonds neither ammonia [1] nor methanol [7,8] dehydrogenates at clean copper surfaces at this temperature and it is likely therefore

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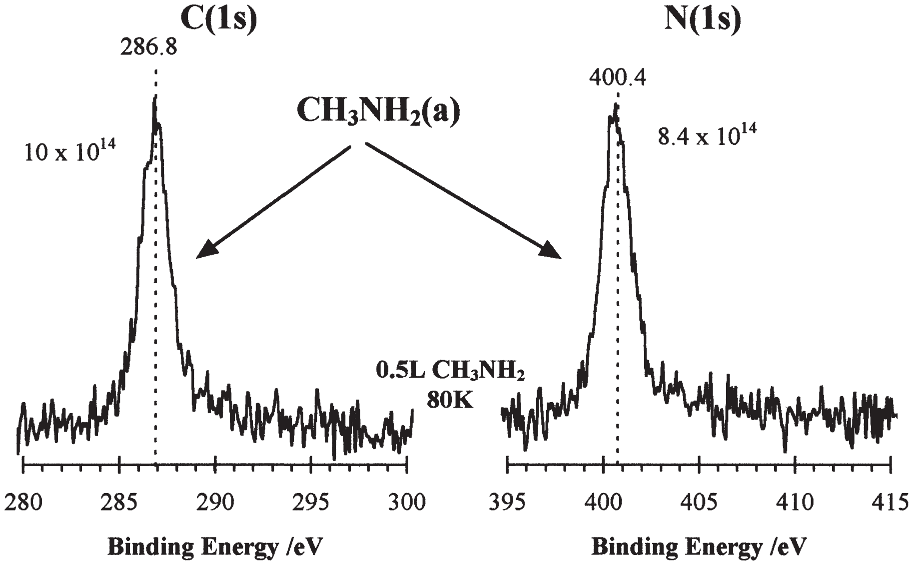

Figure 1. XPS spectra of physisorbed methylamine at a Cu(211) surface following the adsorption of 0.5 L monomethylamine at the clean surface at 80 K. Surface concentrations are shown with units of atoms cm^{-2}.

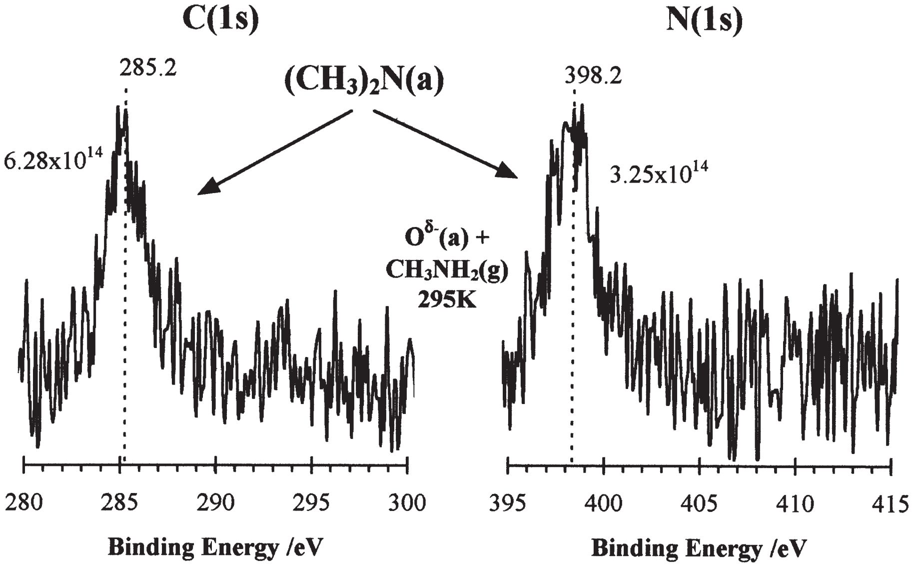

Figure 2. XPS spectra of chemisorbed dimethylamine $(CH_3)_2NH_x$(a) formed after exposing a preoxidised Cu(211) surface ($\sigma_0 = 2.4\times10^{14}$ atoms cm^{-2}) to 12.5 L of monomethylamine at room temperature. Surface concentrations are shown with units of atoms cm^{-2}.

that the amine group remains intact. This is confirmed, on warming, by the complete desorption of the methylamine though in contrast to ammonia (which desorbs from clean copper surfaces at approximately 170 K [1,19]) the monomethylamine does not desorb until ~250 K. The higher heat of adsorption is probably being due to the greater Lewis basicity of the nitrogen atom in methylamine.

3.2. Monomethylamine adsorption at Cu(211) surfaces in the presence of oxygen

The situation is very different when monomethylamine interacts with the Cu(211) surface in the presence of oxygen. In figure 2, N(1s) and C(1s) spectra are shown for an experiment in which a partially oxidised Cu(211) surface ($\sigma_0 \approx 2.4 \times 10^{14}$ atoms cm^{-2}) was exposed to 12.5 L of monomethylamine at room temperature. As in the case of ammonia, exposure to monomethylamine results in the desorption of oxygen and its replacement by a species containing carbon and nitrogen only. In the case of ammonia the oxygen desorbs in the form of water but this is not necessarily the case for methylamine (see discussion below). What is particularly striking about this reaction, however, is the stoichiometry of the nitrogen- and carbon-containing product which we find to be is $1:2 \pm 0.3$ (the error being estimated from repeated experimental observations).

An identical species to that shown in figure 2 is obtained when a clean Cu(211) surface is exposed to a 2 : 1 monomethylamine/dioxygen mixture at room temperature, figure 3. In contrast to ammonia/dioxygen mixtures for

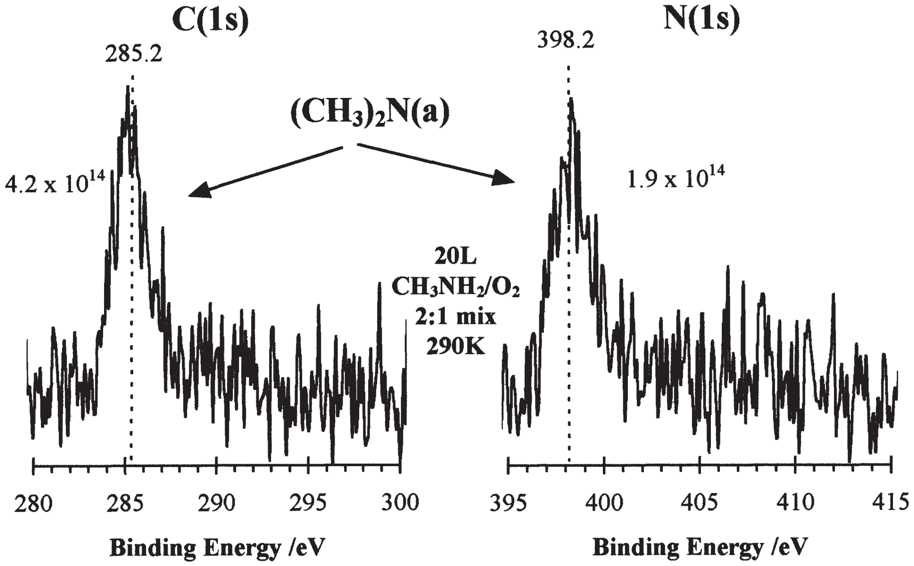

Figure 3. XPS spectra of chemisorbed dimethylamine $(CH_3)_2N$(a) formed when a clean Cu(211) surface was exposed to 20 L of a 2 : 1 methylamine/oxygen mixture at room temperature. Surface concentrations are shown with units of atoms cm^{-2}.

which a 2 : 1 ratio would give both oxide and imide, the 2 : 1 monomethylamine/dioxygen mixture does not leave any oxygen at the surface, only carbon and nitrogen. This can be attributed to the higher heat of adsorption of the methylamine which results in a higher equilibrium coverage during exposure and hence a greater probability that the reactive oxygen transients will encounter methylamine molecules before forming the relatively unreactive oxide [1].

The carbon and nitrogen binding energies of the new species (285.2 and 398.2 eV, respectively), are substantially different from those of the physisorbed methylamine (286.5 and 400.5 eV). The N(1s) bonding energy is closest to adsorbed amide (NH_2, ∼298 eV) but the latter is not stable at copper surfaces above approximately 200 K [1]. The C(1s) binding energy, on the other hand, is significantly higher than that expected for graphitic carbon at this surface (284.5 eV). On the basis of the binding energies and the surface stoichiometry we assign the observed N(1s) and C(1s) peaks to a dimethylamine $(CH_3)_2NH_x$(a), where $x = 0$ or 1.

4. Discussion

The assignment of the carbon- and nitrogen-containing species to dimethylamine $(CH_3)_2NH_x$(a) depends principally on the quantification of the XPS data. The 1 : 1 stoichiometry obtained for the physisorbed monomethylamine (figure 1) gives strong support for the accuracy of this data and there is also considerable evidence in the literature confirming the reliability of stoichiometry calculations from XPS data [18]. In particular correct stoichiometries have been reported for a very large number of adsorbed molecules including NH_2CO_2 [19], CO_3 and CO_2 [20,21], CH_3OH [9], HCO_2 [22], C_5H_6N [23] and 10,11-dihydrocinchonidine [24]. We can therefore have complete confidence in our interpretation of the XPS results.

The 2 : 1 C : N stoichiometry implies the transfer of a methyl group between nitrogen species. Although Freund [25] and Solymosi [26] have independently reported C–C bond formation when CH_3I and CO_2 are coadsorbed at low temperatures, the reaction reported here is unusual because it involves the scission of a relatively strong [12–17] C–N bond. Furthermore, the absence of any decomposition products (C(a) and CH_x(a)) from the methyl group strongly suggests that methyl transfer occurs directly between nitrogen atoms rather than via the metal surface. The only similar case that we are aware of in the literature is the observation in 1962 by Roberts and co-workers [27] of dimethyl sulfide ($(CH_3)_2S$) in the gas phase after nickel was exposed to methyl sulfide (CH_3SH).

Assuming that the relevant oxygen species are chemisorbed atoms (though we cannot rule out molecular oxygen in the case of the coadsorption experiment) we have identified two possible reaction schemes:

$$\begin{aligned}&2CH_3NH_2(a) + O^{\delta-}(a)\\&\quad\rightarrow H_2O(g) + (CH_3)_2NH_x(a) + NH_{2-x}(a)\end{aligned}\tag{1}$$

$$\begin{aligned}&2CH_3NH_2(a) + O^{\delta-}(a)\\&\quad\rightarrow NO(g) + (CH_3)_2NH_x(a) + (4-x)H(a)\end{aligned}\tag{2}$$

Amide (NH_2(a)) is not stable at copper surfaces at room temperature and when formed at lower temperatures dehydrogenates on warming rather than desorbing, hence mechanism (1) should lead to chemisorbed imide and/or nitride. There is no evidence, however, for either species and so if the reaction follows mechanism (1), the amide must desorb from the surface, either as NH_3 after scavenging another hydrogen, or as hydrazine (NH_2NH_2). Neither of these pathways are observed in XPS [1] or TPD [28] studies of the ammonia/oxygen system, however, and we must therefore consider an alternative model which is suggested by the formation [23,29] of a pyridine–oxide complex (C_6H_5N–$O^{\delta-}$(a)) at Cu(111) surfaces. A similar methylamine–oxygen intermediate could lead to the formation of an N–O bond and the subsequent desorption of nitric oxide, mechanism (2). With the data presently available to us, we are unable to discriminate between these two pathways and more detailed investigations designed to resolve this question are currently underway [30].

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