Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 600 (2006) 2364–2371
SURFACE SCIENCE
www.elsevier.com/locate/susc

Reflection absorption infrared study of the adsorption of dimethylamine on copper (1 1 0) and nickel (1 1 1) surfaces

S. Chalker, S. Haq, J.J. Birtill [1], T.S. Nunney [2], R. Raval *

Surface Science Research Centre, University of Liverpool, Oxford Street, Liverpool, L69 3BX, UK

Received 1 February 2006; accepted for publication 28 March 2006

Abstract

The adsorption of dimethylamine on Cu(1 1 0) and Ni(1 1 1) has been studied by reflection absorption infrared spectroscopy. For Cu(1 1 0), adsorption was molecular at 80 and 300 K and for submonolayer dimethylamine the appearance of A′ and not A″ modes indicated C_s symmetry. Similar bonding was found for Ni(1 1 1) at 170 K. Annealing the adlayer to 350 K resulted in the formation of a new species on Ni(1 1 1), similar to that which has been identified as methylaminocarbyne on Pt(1 1 1). In contrast only molecular dimethylamine was identified on Cu(1 1 0), with H-bonded interactions at high coverage and a potential surface dimer.

Keywords: Reflection absorption infrared spectroscopy; Chemisorption; Hydrogen-bonding; Dimerization; Copper; Nickel; Dimethylamine; Methylaminocarbyne

1. Introduction

The interaction of dimethylamine with surfaces is important in a variety of technologies including catalysis, adhesives and microelectronics, yet there have been relatively few surface science studies. There is currently considerable research effort into organometallic alkylamines for the production of oxides, nitrides and arsenides, by means of atomic layer deposition (ALD) and chemical vapour deposition (CVD) [1–4]. Alkylamines are eliminated during these processes, and so their own interactions with surfaces are important. The interaction of dimethylamine with copper has also been studied with regard to the use of amines as curing agents for epoxy resin adhesives in printed circuit board manufacture [5].

Copper and nickel are widely used in catalysis involving dimethylamine. Copper–nickel catalysts are established for the synthesis of fatty amines used for surfactants and corrosion inhibitors, from the reaction of long chain alcohols with alkylamines [6–8]. Alkylamine synthesis from either CO/H_2 or CO_2/H_2 and ammonia occurs over copper catalysts, while nickel, cobalt, platinum and iron produce methane but show little selectivity to alkylamine production [9].

An infrared study of the adsorption of dimethylamine over copper and nickel could reveal differences in the adsorbed species through characteristic group frequencies. There have been two previous vibrational spectroscopic studies of adsorbed dimethylamine on a Cu(1 1 0) surface, both using high resolution electron energy loss spectroscopy, HREELS, but with some differences in the spectra reported and in their interpretation [5,10]. Our study using higher resolution reflection absorption infrared spectroscopy, RAIRS, has been able to distinguish additional subtleties providing further information on the adsorption geometry and enabling some inference on the nature of intermolecular interactions. Kelber and coworkers found molecular adsorption on Cu(1 1 0) at all

---

* Corresponding author. Tel.: +44 151 794 6981.
E-mail addresses: schalker@liv.ac.uk (S. Chalker), R.Raval@liv.ac.uk (R. Raval).

[1] Present address: Department of Chemistry, Joseph Black Building, The University, Glasgow, G12 8QQ, UK.

[2] Present address: Thermo Electron Corporation, The Birches Industrial Estate, Imberhorne Lane, East Grinstead, West Sussex, RH19 1UB, UK.

0039-6028/$ - see front matter
doi:10.1016/j.susc.2006.03.038

temperatures between 100 and 320 K [5]. Similarly, Rao et al. found molecular adsorption of dimethylamine on Cu(1 1 0) at 80 K but suggested that on warming above 120 K, proton extraction by the metal left $(CH_3)_2N$ on the surface [10]. This conclusion relied on the absence of the N–H stretch which has subsequently been explained as due to the intrinsically weak nature of this mode and the orientation of the molecule with the N–H bond parallel to the surface [11]. Molecular desorption was followed with mass spectrometry by Kelber and co-workers [5]. Submonolayer dimethylamine was strongly bound and desorbed at 315 K while additional dimethylamine was less strongly bound and desorbed by 165 K. Multilayers desorbed at 135 K. There can be ambiguity in such thermal desorption studies because recombinative desorption could occur. XPS studies of submonolayer dimethylamine adsorbed on Cu(2 1 1) at 80 K showed only single C1s and N1s peaks, consistent with molecular adsorption, with no change occurring before desorption, between 200 and 290 K [12].

There has been much less work published on the interaction of dimethylamine with nickel. An early study on nickel films was reported by Sheets and Blyholder [13], who found that at room temperature under 30 Torr of dimethylamine, molecular adsorption occurred. Skeletal modes were reported but the νCH region was obscured by the spectrum of the oil on which the films were formed. Although a RAIRS study of the adsorption of methylamine and trimethylamine on Ni(1 1 1) has been previously published [14], we believe this to be the first study of dimethylamine on a well characterised nickel surface.

Finally, few adsorption studies of dimethylamine on other well defined surfaces exist. On Pt(1 1 1), Kang and Trenary found dimethylamine to adsorb molecularly up to around 200 K [11]. Above this temperature abstraction of hydrogen from one carbon atom led to the formation of methylaminocarbyne ($CNHCH_3$) at 350 K. For Si(1 0 0) scission of a C–N bond was proposed for low coverages of dimethylamine at ambient temperature, based on HCN desorption [15] while N–H dissociation was reported for Si(1 0 0) at room temperature, where a νSi–H band was observed [16]. N–H dissociation was also observed for secondary amines over Si at low temperature [17].

2. Experimental

The RAIRS experiments on Cu(1 1 0) were carried out in a stainless steel UHV chamber with a base pressure of 2×10^{-10} mbar. The previously cleaned Cu(1 1 0) crystal was argon ion etched for 20 min at 500 eV and 8 μA, and annealed at approximately 870 K. Auger spectroscopy and low energy electron diffraction were used to check the surface quality. The chamber was fitted with differentially pumped KBr infrared windows and interfaced, via ancillary optics, to an FTIR spectrometer. Infrared spectra were obtained with a single near-grazing reflection from the Cu(1 1 0) surface with the co-addition of 200 scans of a Mattson–Galaxy FTIR spectrometer operated at 4 cm^{-1} resolution and with an MCT detector giving a spectral range of 4000–650 cm^{-1}. The reported spectra are single-beam spectra rationed against a reference background single-beam spectrum from the clean Cu(1 1 0) surface.

The RAIRS experiments for Ni(1 1 1) were carried out in a similar manner, with appropriate cycles of Ar^+ bombardment and annealing to 850 K, in a different chamber and using a Mattson 7020 FTIR, also with an MCT detector and a spectral range of 4000–800 cm^{-1}. Spectra from Ni(1 1 1) were obtained by the co-addition of 400 scans of 4 cm^{-1} resolution.

Dimethylamine of 99+% purity was used as supplied by Aldrich and dosed by backfilling the vacuum chamber through a leak valve. Exposures to dimethylamine are given in Langmuirs where 1 L is 10^{-6} Torr for 1 s. Gas purity was checked using a quadrupole mass spectrometer.

3. Results and discussion

3.1. Symmetry and vibrations of dimethylamine

Dimethylamine has 10 atoms, with 24 normal vibrational modes in the free molecule. The molecule has C_s symmetry, the only symmetry operator being a single mirror plane and is shown in Fig. 1. All of the modes are infrared active in the gas phase, although the strength of the absorption depends on the size of the dynamic dipole. The vibrational modes can be divided into 13 A′ (symmetric with respect to the mirror plane) and 11 A″ (antisymmetric with respect to the mirror plane). The infrared spectrum of gas phase dimethylamine has been studied by Gamer and Wolf [18] and also by Butler and McKean [19]. The solid phase spectrum was reported by Butler and McKean and the frequencies of bands are included in Table 1.

There are three modes associated with N–H: the A′ νN–H stretch at 3000–3500 cm^{-1} and two bending modes, ωN–H, the A′ in-mirror-plane bend at 800–900 cm^{-1} and the A″ δN–H, out-of-plane bend at around 1520 cm^{-1}. Two modes are associated with stretching of the CNC skeleton: the A′ ν_sCNC at 930–990 cm^{-1} and the A″ ν_aCNC at around 1030 cm^{-1}, (the CNC scissors mode occurs around 380 cm^{-1} and is not accessible in these studies). Accessible modes associated with the methyl groups include four rocking modes between 1080 and 1250 cm^{-1},

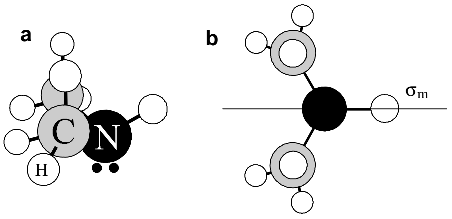

Fig. 1. Diagram of the dimethylamine molecule showing (a) lone pair and (b) mirror plane.