

The adsorption site of ammonia at copper surfaces

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THE ADSORPTION SITE OF AMMONIA AT COPPER SURFACES

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SUMMARY

The adsorption of ammonia at copper surfaces was studied using Hartree-Fock-Slater LCAO calculations to investigate ammonia interaction with copper clusters. Important factors influencing ammonia adsorption were established from trends in its behaviour at clusters of different size. Adsorption at different coordination sites was examined in light of these results and it was found that a strong electrostatic contribution directs the ammonia towards lower coordination sites.

INTRODUCTION

Our interest in the adsorption of ammonia stems from the varied chemistry that has been observed when this molecule is coadsorbed with other species at metal surfaces [1-5]. At a Cu(100) single crystal for instance coadsorption of carbon dioxide with ammonia leads to the formation of a surface carbamate, $\text{NH}_2\text{CO}_2(\text{a})$, [1,2], whilst in the presence of surface oxygen, ammonia undergoes rapid dehydrogenation to give water and a surface amide, $\text{NH}_x(\text{a})$ [3,4]. More strikingly at zinc and silver surfaces there is excellent experimental evidence [5] to show that ammonia can critically influence molecular oxygen transients resulting in an enhancement of the oxygen sticking probability by a factor of up to 10^3 . The aim of the present work is to gain an insight into the bonding of ammonia at metal surfaces in order to give a better understanding of the processes that occur during coadsorption with other species.

There have been several experimental studies of ammonia adsorption at metal surfaces [6-10]. It is generally accepted that the molecule is bound through its nitrogen atom with the C_3 axis perpendicular to the surface plane [9,10]. An analysis of the molecular orbitals of ammonia [11] shows that the highest occupied orbital, the $3a_1$ is concentrated at the nitrogen end of the molecule and ideally suited for sigma interaction. The lowest unoccupied molecular orbital however, the $4a_1$, is concentrated at the hydrogen end of the molecule at a comparatively high energy and would not be expected to contribute significantly to the bonding. The heat of adsorption of ammonia at a Cu(100) surface has been measured at approximately 0.65 eV [6].

There is some debate concerning the adsorption site of ammonia at metal surfaces. Experimental evidence is available for the iridium (111) surface where on the basis of

photoemission results Seabury and co-workers [12,13] suggest adsorption in a three-fold hollow site, and at a Ni(110) surface, [10,14] where ESDIAD results indicate either a two-fold or on-top site. Several calculations have been performed to try to clarify this point. Of particular relevance to the present work are the Constrained Space Orbital Variation calculations of Bagus, Bauschlicher and Hermann who have examined the interaction of ammonia with clusters of 1,5 and 18 copper atoms [15,16]. Their results give an overall attractive interaction of ~ 0.8 eV for the ammonia molecule adsorbed in an on-top position and a repulsive force in the hollow site. They did not examine the bridge site. In contrast, Campbell and Rodriguez using INDO/S to examine adsorption at clusters with 14-18 copper atoms, [17], concluded that the higher coordination sites would be preferred.

At other metal surfaces Bagus et al. suggest a low coordination site for ammonia interaction with aluminium clusters, [18], and Fierro predicts an on-top position for its interaction with platinum clusters using ASED-MO calculations [19]. On the other hand, Chattopadhyay and co-workers [20] found no significant differences in the adsorption energy of ammonia at different nickel sites.

In this paper we present the results of calculations performed for the adsorption of ammonia at five different copper clusters. The clusters represent three different adsorption sites at the copper surface and we also consider the influence of cluster size and geometry on our calculations.

METHOD

Restricted non-relativistic Hartree-Fock-Slater LCAO calculations were made for the adsorption of ammonia at different copper clusters using the HFS-LCAO program implemented by Baerends' group at the Free University of Amsterdam [21-23]. The program allows the adsorption energy to be calculated directly and divided into contributions due to the orbital interaction and to steric effects. The latter can then be further subdivided into terms representing the electrostatic interaction and the exchange repulsion. Basis sets of essentially double zeta quality were used.

The geometry of the ammonia was that of the gas phase molecule [17] and the Cu-Cu distance in the clusters (2.56 \AA), was taken from the bulk metal [18]. Bonding of the ammonia was assumed to be through the nitrogen atom with the molecular axis perpendicular to the surface plane. The Cu-N distance was optimised for the interaction of ammonia with a single copper atom at 2.03 \AA . Calculations were performed on the interaction of ammonia with a single copper atom and with the four clusters illustrated in Figure 1. Three of the clusters considered, Cu(5,4,1), Cu(8,6,2), and Cu(12,6), were chosen to represent the on-top, two-fold bridge and three-fold hollow adsorption sites respectively. The fourth cluster, Cu(1,4,1), was studied because it represents an intermediate stage in cluster development between the single copper atom and the ten atom cluster Cu(5,4,1) and provides an opportunity to examine the influence of cluster size and geometry on the binding energy of the ammonia.

The results of the calculations are shown in Table 1 (total binding energy) and Table 2, (steric effects), where the interaction energy of ammonia with a copper cluster Cu_x , is defined as:-

$$\Delta E_{\text{ADS}} = E(\text{Cu}_x\text{NH}_3) - E(\text{NH}_3) - E(\text{Cu}_x) \quad (1)$$

and so a negative value indicates bonding and a positive value non-bonding.

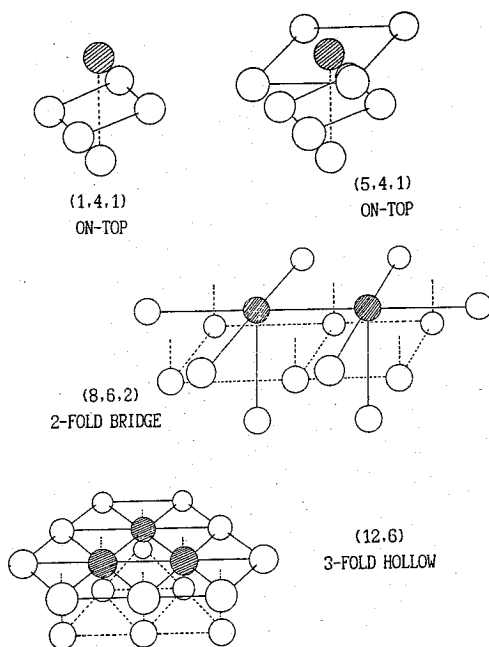


Fig.1. The structures of the four copper clusters studied. Shading indicates atoms coordinated to the ammonia.

RESULTS AND DISCUSSION

From the interaction of ammonia with a single copper atom we get an indication of the important features in the bonding of ammonia to metals. Table 1 shows the orbital interaction between the copper and ammonia to be relatively weak. This is consistent with the simple molecular orbital picture of ammonia where the only significant interaction is expected to be sigma donation from the ammonia to the metal. Opposing the attractive orbital interaction is a

TABLE 1

Contributions to the Total Binding Energy of Ammonia at Different Copper Clusters.

CLUSTER	SITE	STERIC REPULSION /eV	TOTAL ORBITAL INTERACTION /eV	TOTAL BONDING /eV
Atom	-	1.34	-2.19	-0.88
(1,4,1)	On-top	0.38	-1.98	-1.61
(5,4,1)	On-top	0.48	-1.32	-0.80
(8,6,2)	Bridge	0.49	-1.15	-0.67
(12,6)	3-Fold	1.02	-1.29	-0.26

repulsive steric interaction. Contributions to this term, detailed in Table 2, include an electrostatic attraction and a large exchange repulsion. The latter is due to Pauli repulsion between the doubly occupied $3a_1$ orbital of the ammonia, and the copper s orbitals. The electrostatic attraction on the other hand arises from the interaction between the permanent dipole of the ammonia and the positive charge of the copper nucleus together with induced dipole on the copper. The overall binding energy of the ammonia to the copper atom is 0.88 eV, which compares reasonably well with the experimentally determined heat of adsorption of ammonia on Cu(100) of 0.65 eV, [6].

When the cluster size is increased to a six atoms, Cu(1,4,1), Figure 1, the ammonia can be thought of as occupying an on-top site but with only one of the top layer copper atoms present. The orbital interaction between the ammonia and this cluster is very similar to what is observed for coordination to the single copper atom. However, the overall binding energy of the ammonia to the cluster is much larger due to a significant decrease in the steric repulsion of the system. The large change in the steric term can be traced to a reduction in the exchange repulsion, Table 2, which is due to the ability of the central copper atom to polarise charge onto its neighbouring copper atoms and away from the repulsive interactions with the ammonia sigma orbital.

The ability to polarise charge away from the adsorption site of the ammonia leads to an overall binding energy for the ammonia to the six atom cluster that is significantly larger than that calculated for the single atom or observed experimentally for adsorption at a Cu(100) surface, [6]. To explore this further we examined ammonia adsorption in an on-top site on a larger cluster, the ten atom Cu(5,4,1). This cluster gives a more accurate representation of the geometry of an on-top site than does the six atom cluster since the extra four atoms have been added in such a way that they complete the first coordination shell of the copper atom bound to the ammonia molecule, Figure 1.

TABLE 2

Contributions to the Steric Repulsion for Ammonia Adsorption at Different Copper Clusters.

CLUSTER	SITE	EXCHANGE REPULSION /eV	ELECTROSTATIC INTERACTION /eV	STERIC REPULSION /eV
Atom	-	4.8	-3.55	1.34
(1,4,1)	On-top	3.83	-3.45	0.38
(5,4,1)	On-top	4.35	-3.86	0.48
(8,6,2)	Bridge	3.19	-2.70	0.49
(12,6)	3-Fold	4.05	-2.84	1.02

The calculations show that the extra atoms have little effect on the steric repulsion experienced by the ammonia, except for a small increase in the exchange repulsion. They do however give a significant reduction in the orbital interaction term which, because, π bonding is expected to be weak in this system, is probably an effect on the sigma donation of the ammonia. The result is a much lower overall bonding energy and better agreement with the experimental results.

The comparison of clusters Cu(5,4,1) and Cu(1,4,1) as different models for ammonia adsorption at an on-top site, shows clearly the importance of cluster geometry, particularly with regard to the "surface" atoms. In the light of these results the clusters used to represent higher coordination sites were chosen so that each of the two, or three atoms coordinated to the ammonia molecule had a full first coordination shell, Figure 1.

The orbital interaction of ammonia adsorbed in the higher coordination sites is very similar to what is observed when at the on-top site, the major influence on the bonding site is therefore the steric interaction. For both the two-fold and three-fold coordination sites there is a large decrease in the electrostatic attraction experienced by the ammonia compared with the on-top site. This reflects the contribution made to the electrostatics by the attraction between the copper nucleus and the dipole on the ammonia. The results suggest that ammonia will preferentially adsorb at lower coordination sites at copper surfaces. This conclusion is contrary to the work of Campbell and Rodriguez [17] but in agreement with the results of Bagus et al. [15,16]. The difference in opinions probably arises from the superior ability of the LCAO methods to take account of the electrostatic interactions which have been shown here to be important for this system.

CONCLUSION

The bonding of ammonia to copper clusters involves a comparatively weak orbital interaction which is complemented by a strong electrostatic attraction. The results indicate that lower coordination sites are preferred. The importance of cluster size and cluster geometry to

calculations involving ammonia has been demonstrated. Cluster size influences the ability of the coordinated copper atom to polarise charge and reduce Pauli repulsion whereas the orbital interaction depends critically on the first coordination shell of "surface" atoms in the cluster.

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