Molecular Orbital Study on the Interaction of Ni and Cu Atoms with Oxygen-Containing Organic Ligands and Its Implication to Adsorption

Hiroyuki Itoh

Laboratory of Catalysis, RIKEN, The Institute of Physical and Chemical Research, Wako-shi,
Saitama 351, Japan

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The interactions of Ni and Cu atoms with CH_3OH and H_2CO ligands were studied by means of *ab initio* MO calculations. The metal atom-ligand bond length is shorter for Ni than for Cu. Correspondingly, the binding energy is larger for Ni than for Cu. The difference in adsorptive properties of Ni and Cu is explained by the difference in their electronic structures. Alloying effects are discussed. The interaction of the Cu atom with the CH_3O radical is also calculated.

1. Introduction

Extensive studies have been done on gas adsorption on Ni- and Cu-metal surfaces. In the periodic table Cu is next to Ni. The crystal structures of both metals are the same (fcc). Their lattice constants are also very similar. However, their electronic structures are different. Photoelectron spectroscopic experiments [1] did show that, although the top of the 3d band of Ni lies near the Fermi level (E_F), that of Cu lies about 2 eV below E_F. The 4s conduction bands of both metals are considered to be very similar. Their 3d band widths of about 2 eV are much narrower than the conduction band widths.

On the other hand, it is well known that the adsorptive properties such as adsorption energies, work function changes and adsorbed quantities for these metals are also quite different. The present author [2] applied the extended Hückel molecular orbital (EHMO) theory to metal atom clusters of Ni, Cu and alloys of them. The electronic density of states and electronic distributions (Ni $3d^9 4s^1$ and Cu $3d^{10} 4s^1$) are in agreement with the experiments. By the application of this theory to the adsorption of hydrogen and CO on these metals, the difference of the adsorptive properties of Ni and Cu in relation to the difference of their 3d band positions and the similarity of their 4s conduction bands within the orbital interaction scheme was explained [3, 4].

Later *ab initio* MO data for interactions of single transition metal atoms M (Cr, Fe, Co, Ni and Cu) with various ligands (CO, PF_3, H_2O, NH_3, PN, C_2H_2 and C_2H_4) were compared with experimental UPS data for adsorbed systems [5–8]. In these studies the M $3d^{n-1} 4s^1$ electron configuration was assumed because the electron configuration of the transition metal [9] was described as $3d^{n-1} 4s^1$. The 3d and 4s orbital energies of Ni $3d^9 4s^1$ and Cu $3d^{10} 4s^1$ configurations, which were calculated by Clementi and Roetti [10], are listed in Table 1.

Table 1. The 3d and 4s orbital energies (in eV) of Ni $3d^9 4s^1$ triplet- and Cu $3d^{10} 4s^1$ doublet-states [10].

	Ni	Cu
4s	− 6.42	− 6.47
3d	−12.44	−13.35

Although the 4s orbital energies are similar, the Ni 3d energy is about 1 eV higher than that for Cu 3d. The 3d orbitals are very localized compared with the 4s ones. It is well understood that the electronic structures of the bulk Ni and Cu metals as described above result from these properties of the atomic orbitals. Then, it is reasonable to take a single atom as a representation of the metal surface when the electronic properties of Ni and Cu metals in adsorption are examined. In fact, the previous calculations [5–8] compare well with the UPS experiments on adsorption, which show the large downward shift of the HOMO level of an adsorbate when the HOMO level and the metal 4s level have

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Reprint request to Dr. H. Itoh, Laboratory of Catalysis, RIKEN, The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan.

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a net overlap as in the cases of CO, PF_3 and NH_3 ligands.

In this paper the *ab initio* MO method is applied to the interactions of Ni and Cu single atoms with the oxygen-containing organic ligands CH_3OH and H_2CO. The results are compared with corresponding UPS experiments [11–15] on the adsorption of these ligands on Ni and Cu metal surfaces. The method is also applied to the interaction of a Cu atom with an open shell methoxy (CH_3O) group, which is an intermediate of the decomposition of CH_3OH adsorbed on metal surfaces [16]. The effects of alloying of Ni and Cu metals on adsorption are also discussed.

2. Method and Model

The calculations were performed within the *ab initio* restricted Hartree-Fock (HF) approximation. The Ar cores of the Ni and Cu atoms were replaced by effective potentials [17], and their 3d, 4s and 4p-valence orbitals were taken into account by using (2s, 1p, 2d) basis sets according to Wachters [18] and Hay [19]. The contraction coefficients were determined by HF calculations for the respective metal atom with $3d^{n-1}4s^1$ electron configuration. Single zeta basis sets [20] for the ligands were used as in similar previous work [5–8].

The models used are shown in Figs. 1a and 1b for CH_3OH-M and H_2CO-M (M=Ni and Cu) clusters, respecticely. The oxygen atoms of both ligands interact with the M atom. The former is assumed to have a C_s symmetry and the latter a C_{2v} one (linear COM structure). The free molecular geometries for these ligands [21, 22] were used in the present calculations. The O–M distance was optimized to within ± 0.01 Å for a linear COM structure for both clusters. Then, the COM angle for the CH_3OH-M cluster was optimized to within ± 2.5°. For a CH_3O-Cu cluster with C_s symmetry the geometry of a free CH_3OH was assumed for the CH_3O part. The O–Cu distance and the COCu angle were optimized for a closed shell singlet state.

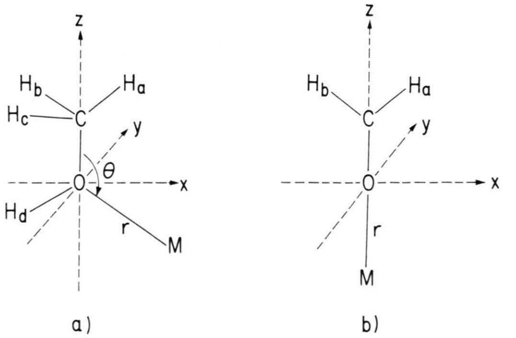

Fig. 1. Models for (a) CH_3OH-M (C_s) and (b) H_2CO-M (C_{2v}) clusters.

3. Results and Discussion

3.1 CH_3OH-M

The theoretical results for the equilibrium OM distance, COM angle, binding energy, CH_3OH like orbital energies and electron populations are represented in Table 2. The equilibrium OM distance is shorter for Ni than for Cu. Correspondingly, the binding energy is larger for Ni than for Cu. The

Table 2. Theoretical data for CH_3OH-M cluster.

a) Equilibrium OM distances, COM angles and binding energies.

	Ni	Cu
r_{eq} (Å)[a]	2.23	2.35
θ (°)[b]	102.5	97.5
E_{bind} (eV)	0.80	0.52

[a] Optimized for a linear COM structure ($\theta = 180°$).
[b] Optimized with use of r_{eq} determined for the linear COM structure.

b) CH_3OH like orbital energies (eV).

Level	Free		Ni	Cu
	Exp. [23]	Theory	Theory	Theory
2a″	−10.94	−12.92	−14.40	−14.06
7a′	−12.68	−13.91	−15.66	−15.38
6a′	−15.19	−17.24	−18.32	−18.04
1a″	−15.7	−18.14	−19.09	−18.83
5a′	−17.50	−19.15	−20.71	−20.36
4a′		−26.15	−26.98	−26.77
3a′		−36.90	−38.49	−38.13

c) Electron populations.

	Free	Ni	Cu
H_a	0.792	0.826	0.838
$H_{b,c}$	0.823	0.816	0.820
C	6.390	6.396	6.391
O	8.525	8.504	8.508
H_d	0.647	0.603	0.612
M		10.039	11.012

reason is that the closed Cu $3d^{10}$ shell, which lies deeper in energy than the partially filled Ni $3d^9$ shell as seen from Table 1, does not contribute to the binding, whereas the very similar Ni $4s^1$ and Cu $4s^1$ orbitals and the open Ni $3d^9$ shell contribute to it. The present results are similar to experiencies on other systems reported before [3, 7]. The COM angle is by 5° larger for Ni than for Cu because of the larger repulsive interaction of the Ni atom with the CH_3O group as seen from the shorter O–Ni distance.

Table 2b shows that the CH_3OH like levels shift towards lower energy with respect to the free CH_3OH levels due to the interaction with the M atom. As seen from Table 2c there is a slight electron transfer from the ligand to the M atom. Then, the M 3d like orbital energies shift by about 1 eV towards higher energy from the free M 3d ones. Reflecting the larger O–Cu distance and smaller electron transfer, the orbital energies of the Cu cluster are nearer to the free CH_3OH values than those of the Ni cluster. In order to compare the calculated results with the UPS experiments of adsorption, however, the energy level separations between the CH_3OH like orbitals must be compared with the experimental values [11–14, 23], as shown in Table 3. The $6a'$ and $1a''$ levels give a single peak in the UP spectra and their orbital energies are averaged. Both experimentally and theoretically the net $2a''-7a'$ level separation increases upon interaction with Ni, although with Cu the experiment [11, 12] and the present calculation give the reverse results. On the other hand, the net $7a'-(6a'+1a'')$ level separation decreases. In this examination it should be noticed that large bonding and antibonding interactions between two orbitals occur when the energy difference between them is small and when the overlap of the two orbitals is large. The HOMO $2a''$ orbital is essentially a pure O $2p_y$ [24], which interacts with the localized M $3d_{xy}$ orbital in the coordinate system shown in Figure 1a. Then, the overlap of them is small and the net downward shift of the $2a''$ is small. However, the second HOMO $7a'$ protrudes outward from the O atom in the xz (COM) plane to make a large positive overlap with the expanded M 4s orbital. Then, its net downward shift is much larger than that of $2a''$. The $6a'$ and $1a''$ levels shift slightly because of the large energy separations between them and the M levels, as seen from Tables 1 and 2b. Consequently, the net $2a''-7a'$ level separation increases, whereas that for $7a'-(6a'+1a'')$ decreases. This kind of orbital interactions was experienced in the $M-H_2O$ systems [7]. The disagreement with the Cu results seems to arise from the procedure in taking a difference spectrum in the UPS experiments.

Table 3. Energy level separations (in eV) between CH_3OH-like orbitals.

	Free		Ni		Cu	
	Exp. [23]	Theory	Exp. [11, 13]	Theory	Exp. [11, 12]	Theory
$2a''-7a'$	1.7	0.99	2.0	1.26	1.3	1.32
$7a'-(6a'+1a'')$	2.7	3.78	2.3	3.05	2.3	3.06

Table 2c shows a slight electron transfer from CH_3OH to the metal atom. Its magnitude is larger for Ni (0.039 e) than for Cu (0.012 e). These results are consistent with the observed work function decreases (−1.6 eV on Ni [13] and −1.35 eV on Cu [12]).

3.2. H_2CO-M

The theoretical results for H_2CO-M clusters are given in Table 4, which shows that the general trend of the equilibrium OM distances and binding energies is similar to that obtained for the CH_3OH-M clusters. As a consequence a similar discussion holds also for the present system.

The UP spectra [23] show a single peak for the $5a_1$ and $1b_2$ levels. The energy level separations of the H_2CO like levels are shown in Table 5. Unfortunately there are only very few detailed UPS experiments of H_2CO adsorption. Only data for Cu [11, 15] are available. Experimentally the $2b_2-1b_1$ level separation decreases upon adsorption on a Cu surface, while the $1b_1-(5a_1+1b_2)$ difference remains constant. Theoretically, however, both level separations remain constant, because with the linear COM model both the $2b_2$ (HOMO) and $1b_1$ levels, which are $2p_x$ and $2p_y$ – like orbitals at the O atom [24], do not interact with the expanded M 4s orbital, but can overlap only with the localized 3d orbitals. Consequently the net level separations should not change. An *ab initio* MO calculation for a H_2CO-Na cluster [25] shows that the Na atom lies above the O atom of the H_2CO molecular plane (CONa angle 90°). Although this calculation suggests a possibil-

Table 4. Theoretical data for H_2CO–M cluster.

a) Equilibrium OM distances and binding energies.

	Ni	Cu
r_{eq} (Å)	2.07	2.56
E_{bind} (eV)	0.34	0.11

b) H_2CO like orbital energies.

Level	Free		Ni	Cu
	Exp. [23]	Theory	Theory	Theory
$2b_2$	−10.9	−13.21	−14.79	−13.94
$1b_1$	−14.5	−16.18	−17.84	−16.96
$5a_1$	−16.0	−18.12	−20.34	−19.06
$1b_2$	−16.6	−20.31	−21.66	−20.98
$4a_1$		−24.24	−25.65	−24.91
$3a_1$		−39.76	−41.22	−40.49

c) Electron population.

	Free	Ni	Cu
$H_{a,b}$	0.818	0.787	0.803
C	6.068	6.015	6.041
O	8.296	8.294	8.290
M		10.118	11.064

Table 5. Energy level separations (in eV) between H_2CO like orbitals.

	Free		Ni Theory	Cu	
	Exp. [23]	Theory		Exp. [11]	Theory
$2b_2-1b_1$	3.6	2.97	3.05	3.1	3.02
$1b_1-(5a_1+1b_2)$	1.6	3.04	3.16	1.6	3.06

ity of non-linearity of the COM angle, more detailed UPS experiments of H_2CO adsorption on Ni and Cu metal surfaces are desirable.

Table 4c shows a slight electron transfer from H_2CO to the M atom. The present result on the Cu cluster is consistent with the observed work function decrease on adsorption (−0.85 eV on Cu) [15]. It is interesting to note here that when the more electronegative atom in the ligands such as CH_3OH, H_2CO, NH_3, H_2O and PN interacts with the M atom, the electron transfer occurs from the ligand to the M atom [7, 8].

3.3. CH_3O–Cu

When the CH_3O group with an open shell electronic structure interacts with a Cu atom with the $3d^{10}4s^1$ configuration, singlet and triplet states are possible for a CH_3O–Cu complex. In this work only the closed shell singlet state is considered. The calculations gave an equilibrium OCu distance of 1.82 Å, a COCu angle of 120° and a binding energy of 1.99 eV. This nonlinearity of the COCu structure is consistent with a conclusion from high-resolution electron energy-loss spectroscopic experiments [16] of a surface CH_3O group on a Ni surface.

The CH_3O-like orbital energies and electron populations at the equilibrium CH_3OCu geometry are shown in Table 6. As can be seen from Table 6b, large electron transfer (0.49 e) occurs from the Cu atom to the CH_3O-group. The transferred electron originates essentially from the Cu 4s level. As a result, the CH_3O-like orbital energies increase drastically in comparison with the free CH_3OH orbital energies shown in Table 2b, whereas the Cu 3d like orbital energies decrease (−14.92 to −15.65 eV) from the neutral Cu atom value of −13.98 eV and lie among the CH_3O like orbital energies. The previous work [26] showed that the relaxation energy associated with the localized 3d shell using the present basis set is very large (about 4 eV). However, it is shown [27] that the ligand levels are reasonably given by Koopmans theorem. Even if this relaxation energy is taken into account, the Cu 3d levels lie below the highest two CH_3O like levels. The 7a′ and 2a″ levels and the 1a″ and 5a′ levels are respectively near degenerate. They become degenerate levels in the linear COCu structure (C_{3v}). Although the experimental UP spectra [14] of the adsorbed CH_3O species are characterized by two peaks in the valence band region, the present calculations do not explain the

Table 6. Theoretical data for CH_3O–Cu.

a) CH_3O like orbital energies (eV).

7a′	− 9.57
2a″	− 9.61
6a′	−12.71
1a″	−16.23
5a′	−16.44
4a′	−23.56
3a′	−32.57

b) Electron population.

H_a	0.849
$H_{b,c}$	0.880
C	6.388
O	8.494
Cu	10.511

experiment as is the case with many HF calculations [27] of transition metal complexes. The reasons of the disagreement may be the closed shell assumption and the neglect of ΔSCF calculations.

4. Conclusion

The difference of the adsorptive properties of Ni and Cu metals is referred to the difference of their electronic structures. Although kinetic studies on the catalytic decomposition of CH_3OH showed a large difference in selectivity between Ni and Cu metals [28, 29], the present calculations do not answer this problem directly. The physical and chemical properties of a metal are determined by the electronic structure near E_F. The existence of 3d holes means that both HOMO and LUMO (E_F) have essentially 3d like character in a chemistry language. The orbital interaction scheme suggests that the directional 3d character (at E_F) of the Ni metal is more convenient to have a net overlap with the CH_3OH orbitals to decompose the molecule than the non-directional 4s character at E_F of Cu. The electrons in a higher energy 3d band are more mobile to transfer to the adsorbate in order to break a bond in the adsorbed molecule as shown in the previous work [5].

Now effects of alloying on adsorption shall be discussed. In the Ni–Cu alloys the 3d band positions of each component metal retain their pure 3d band positions as observed in the UPS experiments [1]. The 4s conduction band is common in the alloy. The Cu 4s electrons do not occupy the 3d hole at the Ni site, irrespective of the alloy composition. The character of the E_F (HOMO and LUMO) of the alloy is both Ni 3d- and 4s-like at the Ni atom site and only Cu 4s-like at the Cu atom site. That is, the properties of gas adsorption are controlled by the local atomic character at the adsorption site. An evidence for this statement is given by a recent UPS experiment [30] of CO adsorption on a Ni–Pt alloy. In fact, the Ni 3d and Pt 5d band positions of the alloy retain the pure metal d band positions. Furthermore, the observed spectrum of CO adsorbed on the alloy is a superposition of the two spectra of CO adsorbed on pure Ni and pure Pt. This experiment shows also that the CO like shifts are larger on Pt than on Ni. This result arises from the facts that [31] the Pt 6s ionization potential (IP) of 8.9 eV is larger than the Ni 4s IP of 7.6 eV and that [32, 33] the Pt 6s and 5d atomic orbitals are much more expanded than the Ni 4s and 3d ones. The Pt 5d IP may be larger than the Ni 3d IP. That is, the CO 5σ and 1π levels interact more strongly with the Pt orbitals than with the Ni orbitals, as will be easily shown by EHMO calculation. A similar situation occurs with the PF_3 complexes of Pt and Ni [34]. The orbital interaction scheme, in which the IP and the extension of the atomic orbital are taken into account, will work in other adsorption system.

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[1] D. H. Seib and W. E. Spicer, Phys. Rev. **B2** 1676 (1970).
[2] H. Itoh, J. Phys. F: Metal Phys. **4,** 1930 (1974).
[3] H. Itoh, Japan. J. Appl. Phys. **15,** 2311 (1976); **16,** 2125 (1977).
[4] H. Itoh, Japan. J. Appl. Phys. Suppl. 2, Pt. **2,** 497 (1974).
[5] H. Itoh and A. B. Kunz, Chem. Phys. Lett. **64,** 576 (1979); **66,** 531 (1979).
[6] H. Itoh, G. Ertl, and A. B. Kunz, Chem. Phys. **59,** 149 (1981).
[7] H. Itoh, G. Ertl, and A. B. Kunz, Z. Naturforsch. **36a,** 347 (1981).
[8] H. Itoh and G. Ertl, Z. Naturforsch. **36a,** 1092 (1981); **37a,** 346 (1982).
[9] L. F. Matheis, Phys. Rev. **134,** A192 (1964).
[10] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14,** 177 (1974).
[11] I. Kojima, H. Sugiura, E. Miyazaki, and I. Yasumori, J. Chem. Soc., Faraday Trans 1, **77,** 1315 (1981).
[12] M. Bowker and R. J. Madix, Surface Sci. **95,** 190 (1980).
[13] G. W. Rubloff and J. E. Demuth, J. Vac. Sci. Technol. **14,** 419 (1977).
[14] J. L. Erskine and A. M. Bradshaw, Chem. Phys. Lett. **72,** 260 (1980).
[15] M. Bouker and R. J. Madix, Surface Sci. **102,** 542 (1981).
[16] J. E. Demuth and H. Ibach, Chem. Phys. Lett. **60,** 395 (1979).

[17] S. Topiol, J. W. Moskowitz, C. F. Melius, M. V. Newton, and J. Faffri, ERDA Res. and Dev. Report (1976).
[18] A. J. H. Wachters, J. Chem. Phys. **52,** 1033 (1970).
[19] P. J. Hay, J. Chem. Phys. **66,** 4377 (1977).
[20] B. Ross and R. Siegbahn, Theor. Chim. Acta **17,** 209 (1971).
[21] R. M. Lees and J. G. Baker, J. Chem. Phys. **48,** 5299 (1968).
[22] K. Takagi and T. Oka, J. Phys. Soc. Japan. **18,** 1174 (1963).
[23] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules (Japan Scientific Societies Press, Tokyo 1981).
[24] W. L. Jorgensen and L. Salem, The Organic Chemist's Book of Orbitals, Academic Press, New York 1973.
[25] F. Bernardi, G. Pedulli, M. Guerra, and H. B. Schlegel, Gaz. Chim. Ital. **105,** 711 (1975).
[26] H. Itoh, Z. Naturforsch. **36a,** 1095 (1981).
[27] E. P. F. Lee, A. W. Potts, M. Doran, I. H. Hillier, J. J. Delaney, and M. F. Guest, J. Chem. Soc. Faraday II, **76,** 506 (1980).
[28] E. Miyazaki and I. Yasumori, Bull. Chem. Soc. Japan. **40,** 2012 (1967).
[29] I. Yasumori, T. Nakamura, and E. Miyazaki, Bull. Chem. Soc. Japan. **40,** 1372 (1967).
[30] Y. Jugnet, J. C. Bertolini, J. Massardier, B. Tardy, T. M. Duc, and J. C. Vedrine, Surface Sic. **107,** L320 (1981).
[31] R. F. Bacher and S. Goudsmit, Atomic Energy States, McGraw-Hill, New York 1932.
[32] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38,** 2686 (1963).
[33] E. Clementi, D. L. Raimondi, and W. P. Reinhardt, J. Chem. Phys. **47,** 1300 (1967).
[34] A. H. Cowley, Progr. Inorg. Chem. **26,** 45 (1979).