THE BONDING PROPERTIES OF CARBON MONOXIDE ADSORBED ON METALS*

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From the EHMO calculations, backbonding has been found to be the main contributing factor for C − O bond weakening, when CO adsorbs over Ni and Cu. The available EELS stretching frequency data are used to calculate the C − O bond energy at various coverages of CO on Pt, Ni, Ru and Pd. The increase in bond energy with increasing coverage in these cases also indicates that backbonding is the main contributing factor for C−O bond weakening.

1. INTRODUCTION

The study of activation of CO on metal surfaces has gained importance due to its behaviour as a model for adsorption phenomenon as well as due to its relevance for industrially or otherwise important reactions like Fischer-Tropsch synthesis, methanation and auto-exhaust conversion reactions [1 − 3]. CO adsorbs on metals in a configuration wherein its molecular axis is parallel to surface normal and the carbon atom is nearer to the surface. The bonding occurs by the electron transfer from 5σ orbital of CO to the unoccupied metal 'd' states, accompanied by the backdonation of electrons from the occupied 'd' states of the metal into the empty antiboding 2π orbital of CO. UPS, work function measurements and vibrational spectroscopy are some of the methods by which information on the magnitude of backdonation by transition metals and the resultant weakening of the C−O bond can be obtained [4−6]. It has been noticed that the observed stretching vibration frequency of adsorbed CO is always lower than that of gaseous CO, indicating the weakening of C−O bond due to adsorption. It is conceived that this weakening of C−O bond is due to various reasons like backdonation (the population of the antibonding 2π orbital of CO with metal 'd' electrons), vibronic coupling between coadsorbed species, dipole-dipole coupling at higher coverages, dipole coupling with its image dipole in the metal and mechanical effects at low coverages.

The present communication deals with
 i) the analysis of reasons for weakening of C−O bond, on adsorption of CO over transition metals by performing Extended Huckel Molecular Orbital (EHMO) calculations and
 ii) the analysis of the backbonding properties of some metals at various surface coverages of CO, from the available Electron Energy Loss Spectral (EELS) data reported in literature on smooth surfaces like FCC (111) and (100) planes of metals where dissociation is small compared to open and stepped surfaces [7].

2. METHOD

EHMO calculations have been carried out for CO adsorption on 7-atom clusters of nickel and copper representing Ni(111), Ni (100) and Cu (100) surfaces. The geometry of the metal clusters and the sites of adsorption of CO were chosen on the basis of experimentally observed LEED patterns [8]. Metal-metal distances were considered to be the same as in the bulk metal. Metal-carbon and carbon-oxygen distances used were 1.84Å × 1.150Å for nickel and 1.905 Å × 1.150 Å for copper respectively. The other required parameters namely Valence Orbital Ionisation Energies (VOIE) and orbital exponents were taken from Refs. [9] and [10] respectively. From the reported stretching frequencies of adsorbed CO on various metals, the force constant and C—O bond energy were computed by the method reported by Chang [11].

3. RESULTS AND DISCUSSION

3.1. EHMO CALCULATIONS

Binding energies obtained from EHMO calculations for Cu_7 and Ni_7 clusters with one and two CO molecules are given in Table 1. The binding energy is not altered significantly by the adsorption of a second CO molecule on nickel cluster, but in the case of Cu there is a considerable decrease in the binding energy due to the adsorption of the second CO.

Table 1

Binding energies for adsorption of CO molecule on metal clusters

Cluster	Binding energy(eV)
$Ni_7CO(111)$	5.46
$Ni_7(CO)_2(111)$	5.36
$Ni_7CO(100)$	5.21
$Ni_7(CO)_2(100)$	5.27
$Cu_7CO(100)$	4.12
$Cu_7(CO)_2(100)$	2.84

Table 2

Calculated band widths (eV) for the valence levels of CO

CO molecular levels	$Ni_7(CO)_2$ (111)	$Cu_7(CO)_2$ (100)	$Ni_7(CO)_2$ (100)
5σ	0.07199	0.03698	0.0411
1π	0.01717	0.00363	0.0046

The reason for this behaviour is derived from the analysis of the molecular orbitals obtained from the EHMO calculations. In the case of Ni, the backdonation of electrons to the 2π level of CO occurs from the d band which has a high occupied density of states at an energy above the 2π level of CO. Therefore, the backdonation does not decrease with the addition of a second CO molecule. On the other hand the backdonation to the 2π level occurs from the sp band in the case of Cu, which does not have a high occupied density of states at energies above the 2π level. Therefore the backdonation to the 2π level decreases with the addition of second CO molecule. There is not much of direct interaction among the coadsorbed molecules. Recent reports of similar calculations to find the interaction between coadsorbed CO on Rh(111) by Ruckenstein and Halachev [12] also indicate that the interaction among the coadsorbed species is very weak and it is of the order of a few hundreds of an eV.

There is a delocalisation of molecular orbitals of CO as indicated by the finite band width for the CO valence levels when two CO molecules are over 7-atom metal clusters as seen from the values given in Table 2. However, it may be concluded that backdonation is the main contributing factor for weakening C—O bond compared to the vibronic coupling etc.

3.2. ANALYSIS OF EELS DATA

Table 3 shows the spectral frequencies and the calculated parameters at various coverages of CO on some metals. From these results, it is observed that at low coverages, CO binds strongly to the surface and the

Table 3

Experimental EELS data and calculated properties for the adsorption of CO on metals

System	Exposure or θ	ν_{C-O}[a] cm^{-1}	$F \times 10^{5}$[b] dyne/cm	E_{C-O}[c] kcal/mol	ΔE[d] kcal/mol	Ref.
Gaseous CO	—	2170	19.02	257	—	[11]
CO/Pt(111)	0.20<	2090	17.64	238	19	
	0.40<	2098	17.78	240	17	[14]
	1.00<	2106	17.91	242	15	
CO/Ni(110)	0.10	1855	13.90	188	69	
	0.40	1879	14.26	193	64	[15]
	0.65	1904	14.64	198	59	
	0.95	1944	15.26	206	51	
CO/Ru(001)	0.02	1985	15.91	215	42	
	0.10	2000	16.15	218	39	
	0.20	2010	16.32	220	37	
	0.33	2017	16.43	222	35	[16]
	0.40	2030	16.64	225	32	
	0.50	2038	16.77	227	30	
	0.60	2046	16.91	228	29	
CO/Pd(100)	0.03	1775	12.72	172	85	
	0.07	1800	13.08	177	80	
	0.14	1830	13.52	183	74	
	0.18	1830	13.52	183	74	[17]
	0.25	1852	13.85	187	70	
	0.36	1905	14.66	198	59	
	0.50	1905	14.66	198	59	
	0.68	1941	15.21	205	52	

[a] — stretching frequency of adsorbed CO
[b] — Force constant calculated from ν_{C-O}
[c] — Energy of the C—O bond for adsorbed CO
[d] — Difference in bond energy between gaseous CO and adsorbed CO

C—O bond weakening is maximum. As the coverage increases, the C—O bond energy increases and approaches the value of gaseous CO. The salient results arising out of the analysis of adsorption of CO on various metals are :

i) The relative contribution of backdonation for various metals is revealed. It is greater for metals like Ru, Ni and Pd while it is the least in the case of Pt. A similar variation has been observed in the work function changes too [6]. This effect has been probed from the correlation of the charge transition energy with the heat of adsorption [13].

ii) It is normally believed that the displacement of 5σ electron density towards the metal is occurring to a greater extent than the displacement of metal 'd' electrons to 2π orbital of CO. The support for this argument comes from the fact that there is no simple correlation between the heat of adsorption and the shift in vibration frequency at various coverages of CO on Pd (Table 4). The observations that the heat of adsorption, ΔH, as a function of θ varies almost linearly with ΔE and the difference between these two quantities is almost constant up to $\theta = 0.4$ (Table 4), indicate that the backdonation is the strong contributing factor for the weakening of C—O bond of CO on adsorption over metals.

Table 4

Experimental high resolution IR stretching frequency[τ] and calculated properties for the adsorption of CO on Pd (100)

θ	v_{C-O}[a] cm^{-1}	$F \times 10^{5}$[b] dyne/cm	E_{C-O}[c] kcal/mol	ΔE[d] kcal/mol	ΔH[e] kcal/mol	$(\Delta E - \Delta H)$ kcal/mol
0.10	1907	14.69	198.5	54.5	34.6	19.9
0.20	1913	14.79	199.8	53.2	32.5	20.7
0.30	1921	14.90	201.3	51.7	30.6	21.1
0.40	1928	15.01	202.8	50.2	29.4	20.8
0.47	1947	15.31	206.8	46.2	28.0	18.2
0.50	1951	15.37	207.6	45.4	22.0	23.4

[τ] — values collected from : A. M. Bradshaw and F. M. Hoffmann. Surface Sci., **72**, 513 (1978).
[a] — stretching frequency of adsorbed CO
[b] — Force constant calculated from v_{C-O}
[c] — Energy of the C—O bond for adsorbed CO
[d] — Difference in bond energy between gaseous CO and adsorbed CO
[e] — heat of adsorption

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