

MECHANISM OF HYDROGENATION OF CARBON MONOXIDE OVER FERROUS METAL CATALYSTS: CLUSTER CALCULATION BY EHMO METHOD

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Summary

The observed product selectivities in the hydrogenation of CO on Fe, Co and Ni is rationalised through Extended Huckel Molecular Orbital (EHMO) cluster calculations for the various surface species that can be formed during the reaction.

Introduction

One approach of surface science research toward understanding the catalytic properties of solid surfaces is the study of clusters of atoms which can mimic the surface [1]. Cluster calculations provide information on the required number and geometry of surface atoms and crystallite size for a specific reaction to occur. The properties of these clusters determine the initial mode of adsorption of reactants, and thus control the path of the reaction.

The importance of activation of carbon monoxide as a prototype in cluster modelling studies has been brought out [2] in relation to its relevance in oxidation for auto exhaust control reactions and reduction for production of syngas as well as organic chemicals.

Though reports [3] on the theoretical study of adsorption of carbon monoxide on ferrous metals (Fe, Co and Ni) are available, there has been no unified attempt using a single calculation technique on similar planes of these metal surfaces. Further, no attempt has been made to elucidate the mechanism of hydrogenation of carbon monoxide on these surfaces through cluster calculations. In earlier studies [4] on the interaction of carbon monoxide and hydrogen on the clusters of ferrous metals, important clues to possible intermediates were obtained. However, the mode of adsorption, the relative strength of bonding of CO on these metals, the ease of dissociation and hydrogenation and the relative stability of various hydrogenated species seemed to be decisive for the product distributions observed. Hence, in the present study, electronic properties of clusters representing the adsorption

of carbon monoxide and relevant carbon-containing species on ferrous metals are calculated in order to rationalise the product distribution.

Method

The Extended Huckel Molecular Orbital (EHMO) method [5] has been used with Slater type orbitals (STO — single — ζ functions). The detailed procedure of calculation is explained elsewhere [4a]. Adsorption energy is calculated as the difference between the total energy of the system and the sum of atomic energies of all individual atoms by making use of expression (1):

$$\text{Adsorption energy} = \sum_{\text{SC}} n_i^{\text{SC}} E_i^{\text{SC}} - \sum_{\text{S}} n_i^{\text{S}} E_i^{\text{S}} - \sum_{\text{g}} n_i^{\text{g}} E_i^{\text{g}} \quad (1)$$

where SC is surface complex, S is adsorbent and g adsorbate, E_i is the orbital energy, $n_i = 0, 1$ and 2 depending upon occupancy of orbitals. Summation is over all atoms of the concerned state.

The method is parameterised to obtain near-to-accurate SCF wave functions, and hence further-derived properties such as MO energy levels and atomic overlap population are fairly quantitative. Though the adsorption energy and values of formal charges are a little higher than the absolute values, due to the neglect of core electron effects and electron-electron repulsion effects, the trends predicted are useful for comparative evaluation and hence this is attempted in the present study. The required input parameters such as valence orbital ionisation energies (VOIEs) [6] and orbital exponents [7] are collected from the same source for all elements.

Results and discussion

Adsorption of carbon monoxide

It has been shown that the bonding of carbon monoxide to metals occurs through the carbon atom. The 5σ electrons of carbon monoxide are used to form an M—C σ bond and this weakens the C—O bond [8]. In addition, the metal d electrons are transferred to the lowest unoccupied molecular level of carbon monoxide, namely the $2\pi^*$ antibonding orbital, thus leading to a further decrease in the C—O bond order in the adsorbed state. Carbon monoxide adsorbed in the linear mode (over a single metal atom M—C—O; on top) as well as the bridged mode (over two metal atoms

$\begin{array}{c} \text{M} \\ \diagdown \\ \text{C—O} \\ \diagup \\ \text{M} \end{array}$) over the clusters representing basal planes of ferrous metals are studied.

Typical geometries used for model calculations are given in Fig. 1, and the values of the interatomic distances used are given in Table 1. Though Fe,

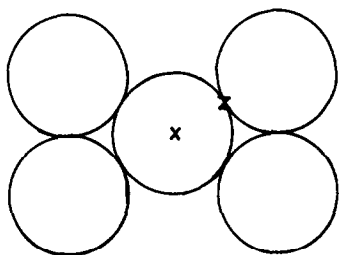


Fig. 1. Typical model cluster chosen to represent (100) plane of fcc metal (Ni) on top site (x) and bridge size z (similar crystal geometries were chosen for bcc and hcp metals).

TABLE 1

Cluster models chosen for basal planes of ferrous metals

Metal	Crystal Lattice	Number of atoms in cluster	Geometry	Symmetry	Metal-metal distance (Å)	Metal-carbon distance (Å)
Fe	bcc	5	square pyramidal	C_{4v}	$a_o = 2.8664$	1.797
Co	hcp	7	hexagonal planar	D_{6h}	$a_o = 2.5074$ $c_o = 4.0699$	1.80
Ni	fcc	5	square planar	D_{4h}	$a_o = 3.5238$	1.84

Co and Ni resemble each other in many of their physical properties, they exist in different crystal lattices and the cluster model chosen to represent their basal planes are also shown in Table 1. The binding energies and other calculated parameters for adsorption of CO on the clusters shown in Table 1 are given in Table 2.

The values of the binding energies show that the strength of adsorption of carbon monoxide to these metals is in the order $Fe > Co > Ni$. It is also seen that the bridged mode of adsorption is energetically more favourable than the linear mode of adsorption in all cases. In the case of Ni(100), experimental evidence is available [9] for the presence of both Ni_2CO and $NiCO$ species on the surface. Anderson [10] also showed the presence of bridge-bonded CO on Ni(100) by EELS studies. Bridge *et al.* [11] have shown the presence of both modes of carbon monoxide adsorption on the Co(1000) surface at room temperature from the results of their LEED studies. The observed coexistence of both linear and bridged modes of adsorption of carbon monoxide on these surfaces is understandable, since the difference in their calculated adsorption energy is marginal. However, in the case of the Fe(100) surface, since the cluster is non-planar, carbon monoxide interacts with all four metal atoms on the top layer. Though the degree of bonding of M-C bond is less (0.457), the actual value is four times higher due to its equal interaction with four metal atoms. Rhodin and Brucker [12] have also shown that molecular adsorption of carbon monoxide on the Fe(100) surface is on a 4-fold site at 123 K, and dissociation occurs at 300 K.

TABLE 2
Various calculated parameters for adsorption of CO on ferrous metals

Cluster properties	C-O ^a	CO adsorbed in linear mode on			CO adsorbed in bridged mode on		
		Fe(100)	Co(1000)	Ni(100)	Fe(100)	Co(1000)	Ni(100)
Adsorption energy (eV)	11.484	18.561	8.439	6.589	20.370	9.112	7.830
Electronic energy levels	4σ	-20.544	-20.541	-20.541	-20.585	-20.577	-20.570
	1π	-18.367	-18.347	-18.345	-18.303	-18.354	-18.350
	1π	-18.367	-18.299	-18.347	-18.301	-18.350	-18.347
	5σ	-14.453	-15.330	-15.349	-15.706	-15.551	-15.463
Metal	4s	-10.352	-10.058	-10.058	-10.763	-10.453	-10.114
	2π	-9.158	-10.084	-10.030	-9.709	-10.260	-10.185
Degree of bonding between	2π	-9.158	-10.084	-10.030	-9.709	-9.674	-9.733
	C-O	1.832	0.928	0.910	0.943	0.911	0.926
	M-C		0.457	0.855	1.151	0.999	0.887
Formal charges on atoms	M-O		0.030	0.032	0.066	0.054	0.043
	C	1.002	-1.509	-2.018	-1.609	-1.426	-1.727
	O	-1.002	-1.410	-1.464	-1.410	-1.457	-1.445

^aThe energy is simply the atomization energy.

Weakening of the C—O bond due to adsorption of carbon monoxide can be noted from the values of degree of bonding for the C—O bond. The degeneracy of 1π and 2π orbitals are not affected for the linear mode whereas it is disturbed for the bridged mode, indicating a stronger interaction.

It seems that the strength of adsorption of carbon monoxide critically depends on the geometry of atoms in the cluster. The structural sensitivity of adsorption and further reaction of carbon monoxide has also been pointed out in a recent study by Fu and Bartholomew [13]. In the hydrogenation of carbon monoxide, when the dispersion of metals is varied by changing the preparation procedure, the average carbon number of the products also varies. Highly dispersed catalysts where high coordination sites are not available lead to low molecular weight hydrocarbons, showing that low coordination sites do not favour chain initiation but lead to chain termination. In general, one can consider dissociation of carbon monoxide leading to carbide-type species as chain initiation, C—C bond formation as chain propagation, and C—H bond formation as chain termination processes. The results cited above can be taken to indicate that the presence of high coordination sites is a pre-requisite for strong adsorption and dissociation of carbon monoxide. This is also predicted by the calculations that strong adsorption takes place in the case of iron, where multiple-site interaction is possible.

Formation of carbide and one-carbon intermediates

Carbon monoxide dissociates over ferrous metals at the higher temperatures at which hydrogenation is carried out. Adsorption energies of the individual elements carbon, oxygen and hydrogen, as well as possible one-carbon intermediates such as $-\text{CH}$, $-\text{CH}_2$ have been computed, and are given in Table 3.

The adsorption energies of these species are in the same trend as the adsorption energy of carbon monoxide. However, in the case of iron, a carbide layer has been identified even in the presence of hydrogen [14], but no such carbide layer was found over cobalt and nickel in presence

TABLE 3

Binding energies (in eV) of various species on basal planes of ferrous metals in linear and bridged modes

Mode of adsorption and adsorbent	Adsorbed species				
	H	O	C	CH	CH ₂
linear mode on Fe(100)	16.47	31.65	23.85	27.82	28.79
bridged mode on Fe(100)	18.73	31.53	24.94	28.31	30.11
linear mode on Co(1000)	5.38	20.53	14.71	17.10	17.21
bridged mode on Co(1000)	4.26	19.40	14.34	17.00	16.97
linear mode on Ni(100)	4.06	18.90	12.48	15.75	16.32
bridged mode on Ni(100)	4.98	18.81	13.18	16.05	17.13

of hydrogen [15]. Hence it is obvious that hydrogenation of carbide species over these metals takes place in a facile manner and causes the difference in their selectivity.

Due to the simultaneous occurrence of different reactions and because of the labile nature of bonds in surface intermediates, it is difficult to evaluate the energetics of individual steps by experimental methods. However, since the adsorption energy of individual species are known by calculation, it is possible to calculate the energy required for formation of hydrogenated one-carbon intermediates. The ease of formation of partially hydrogenated species is calculated by deducing the binding energy of the species from the sum of binding energies of the individual elements. Energetics of formation of $-CH$ and $-CH_2$ species are given in Table 4. It is observed from the values

TABLE 4
Energy of formation of one-carbon intermediates

Surface and mode of adsorption	E_f of $-CH$ (eV)	E_f of $-CH_2$ (eV)
Fe(100) linear	12.5	28.0
Fe(100) bridged	15.36	32.29
Co(1000) linear	3.00	8.28
Co(1000) bridged	1.61	5.90
Ni(100) linear	0.78	4.28
Ni(100) bridged	2.11	6.01

in Table 4 that the formation of $-CH$ species is easier than $-CH_2$. However, it is likely that $-CH$ gets converted to $-CH_2$, rather than the direct formation of $-CH_2$ occurring from individual elements. These values also indicate that the ease of hydrogenation of the carbide layer is in exactly the reverse trend to the ease of carbide formation over the ferrous metals. Two vital processes are involved in the mechanism of carbon monoxide reduction, namely, dissociation of carbon monoxide to give surface carbide and hydrogenation of these carbide species. Knowing the energetics of these two

TABLE 5
Distribution of products obtained during the hydrogenation of CO on ferrous metals [16]

Metal catalyst	Product distribution (%)		
	Paraffin	Olefin	Alcohol
Fe	46.4	33.1	20.5
Co	79.0	20.0	1.0
Ni	100.0 (90% CH_4)	—	—

processes makes it possible to conclude the reasons for the observed selectivity over ferrous metals shown in Table 5.

Conclusions

(i) On iron, dissociation of carbon monoxide is more facile than hydrogenation. Hence chain propagation occurs by C—C bond formation leading to hydrocarbons, or by CO insertion leading to oxygenates.

(ii) On cobalt, both dissociation and hydrogenation occur. This leads to C—C bond formation and hydrogenation. It appears that hydrogenation is relatively favourable, so that there is no CO insertion.

(iii) On nickel, dissociation is not so facile as hydrogenation, so that there is no C—C bond formation or CO insertion, nor partial hydrogenation leading to olefins or alcohols in the product.

The results obtained indicate that the required selectivity can be achieved by alloying these metals in the optimum proportions. Studies on clusters representing multiple adsorption and on other planes of these metals can provide an overall picture of the relative importance of various modes of adsorption and geometry of clusters for this reaction. This can help predict the optimum metal particle size required in supported catalysts, and also can indicate the cluster size requirements in novel homogeneous and anchored catalysts currently being used for activation of carbon monoxide.

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