ADSORPTION OF CARBON MONOXIDE ON THE IRIDIUM fcc (112) SURFACE: TOPOLOGICAL STUDY

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A semi-empirical topological method was applied to a study of an Ir(112) surface as well as to both a nondissociative and dissociative chemisorption on this surface. In all cases studied an attachement of carbon to the surface is energetically more favorable than an attachement of oxygen. The preferential capture of the CO molecule on atop sites is remarkable. The capture on *n*-fold hollow positions as well as the dissociative chemisorption of carbon monoxide on the Ir(112) surface are energetically prohibited.

An adsorption of gases on transition metal surfaces has been studied in many papers. There were two reasons for such studies. Many transition metals exhibit a strong catalytic activity the adsorption being the first step in a chemical reaction. Therefore, the study of relations between the structure and their adsorption ability can give some insight into the catalytic activity.

Recently we have developed[1] a simple quantum chemical method which enables us to study large molecular systems. In our recent paper[2] we applied this method on calculations of both dissociative and nondissociative chemisoprtion of CO on Ni and Cu surfaces. In this study, we report an adsorption of CO on the iridium surface. It is well known experimentally[3-10] that iridium has quite different adsorption properties than either nickel or copper. The nondissociative adsorption was only found and therefore no catalytic activity has been observed on Ir surfaces unlike a nickel behavior. In most experiments atop adsorption has been the only one observed on low index planes and at low coverages. Theoretical papers dealing with the adsorption of CO on Ir are very scarce[11-18].

THEORETICAL

In this paper the same computational method has been used as in previous papers[1,2] and we refer to them for details. It is essentially a topological method based on the one-center Hamiltonian in which resonance integrals were calculated between all pairs of equivalent orbitals which belong to the nearest neighbor atoms. Coulomb

integrals were approximated by scaled orbital electronegativities (cf. Table I), resonance integrals were calibrated on heats of formation of small systems. For resonance integrals between equivalent orbitals oriented toward nuclei, values -131.8, -103.2, and -82.7 kJ/mol for Ir—Ir, Ir—C, and Ir—O were selected. Similarly as in ref.[2] resonance integrals for Ir—C and Ir—O bonds on many-fold sites were reduced to -22.9 and -18.3 kJ/mol by using Morse function based on experimental data for the experimental distances.

The metal crystal consisted of 27 iridium atoms and periodic boundary conditions were satisfied by a formation of a torus (cf. ref.[2]). By appropriate linking nine elementary (112) crystal planes were obtained. (The (112) plane was selected since it is the lowest index plane which exhibits step.) A list of all positions for which the nondissociative adsorption was calculated is presented in Fig. 1. Letters A and B place a linear CO molecule perpendicularly to a step or a terrase, respectively. A list of all positions for which the dissociative adsorption was calculated is presented in Figs 2—3.

RESULTS AND DISCUSSION

As has been said previously, the torus represents an infinite crystal with nine elementary (112) planes. Due to the conservation of the translational symmetry atoms in respective planes are identical. Calculated charge densities and bond orders for Ir atoms in various planes are presented in Table II. Bond orders are tabulated only for atoms lying in the same plane. The positive charge was concentrated entirely on the surface of the Ir crystal. This fact is contrary to the behavior of Ni and Cu crystals[2]. The positive charge are mainly located in the first surface layer.

An energy of nondissociative chemisorption (energy gain) of the process

$$
\begin{array}{c}
\text{O} \\
| \\
\text{C} \\
| \\
\text{Me} + (\text{CO})_g \quad \rightarrow \quad \text{Me}
\end{array}
\qquad (A)
$$
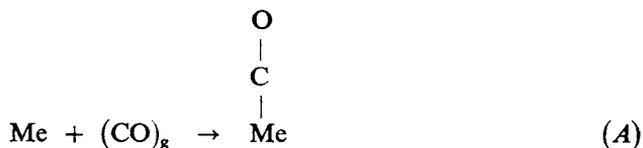
and a total amount of charge on carbon monoxide are summarized in Table III. The stability of the chemisorption complex decreases in the order IV > V > VI ≫ ≫ I > II > III.

Note that there is a particularly strong adsorption at the top position. The n-fold hollow positions I, II, III will predominate in agreement with experimental findings on low index planes such as (100), (110), and (111) (refs[3-10]).

The amount of a charge transferred between the metal crystal and CO strongly depends on the type of a respective adsorption site. Adsorption on atop positions is followed by an electron donation from CO to the metal.
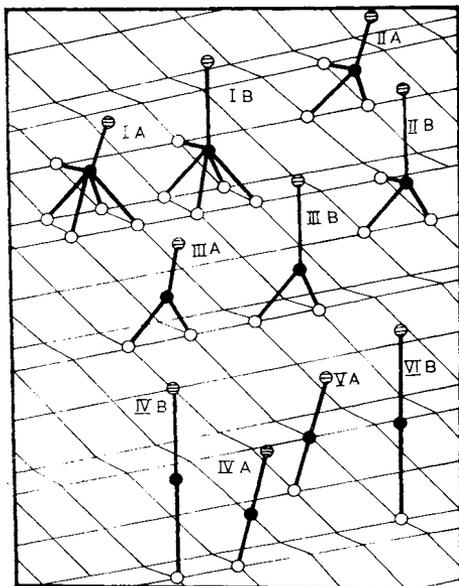
FIG. 1

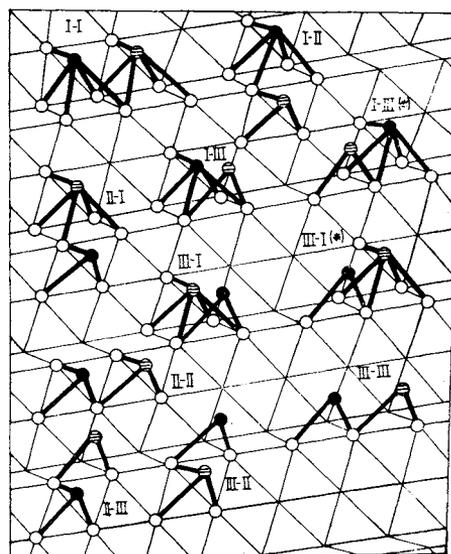The list of linear CO capture studied in this paper, ● and ⊖ stand for C and O atoms, resp.

FIG. 2

The list of dissociative CO captures between n-fold hollow centers studied in this paper, ● and ⊖ stand for C and O atoms, resp.
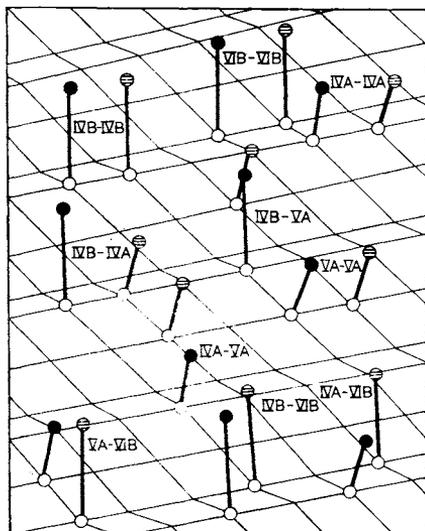

FIG. 3

The list of dissociative CO captures between on top centers studied in this paper, ● and ⊖ stand for C and O atoms, resp.

The dissociation ability of the adsorbed molecule can be described qualitatively by the change of the CO bond order in the course of the adsorption process. It is seen in Table III that the bond weakening is about 3 to 4 times larger for top systems as compared with the n-fold hollow systems. This finding indicates the principal change in a reactivity of CO in the top positions. Adsorption energies for a capture on an oxygen side are substantially lower than those for the Me···CO adsorption. Therefore the adsorption Me···OC can be ruled out.

Chemisorption energies for the process

$$
\begin{array}{ccc}
 & & \text{C} \quad \text{O} \\
 & & | \quad\; | \\
\text{Me···Me} + (\text{CO})_g & \rightarrow & \text{Me···Me}
\end{array} \qquad (B)
$$

as well as sum of charges on carbon and oxygen are presented in Table IV. The

TABLE I
Mulliken's orbital electronegativities for the elements under study in kJ/mol

Element	s	p	d	f
Ir	−655	−251	−872	0
C	−1 473	−597	−108	0
O	−2 507	−991	−158	0

TABLE II
Charge densities q and bond orders p on the subsequent planes of the metal torus

Plane	q	p
1	0·22	1·36
2	0·07	0·85
3	−0·16	0·78
4	−0·12	0·67
5	0·03	0·75
6	−0·12	0·67
7	−0·16	0·78
8	0·07	0·85
9	0·22	1·36

actual orientations of C and O atoms are displayed in Figs 2 and 3. It is seen that all chemisorption energies are several times less than those for linear captures, thus the dissociative adosprtion on this surface seems to be ruled out. The tentative explana-

TABLE III

Adsorption energies E_{ad} in kJ/mol, total charges Q of adsorbed molecules and relative bond order changes $-\Delta p$ on CO bonds for all systems under study. The respective systems are displayed in Fig. 1

System	Capture of C			Capture of O		
	E_{ad}	Q	$-\Delta p$	E_{ad}	Q	$-\Delta p$
IA	−107	0·0662	0·2365	−142	0·0544	0·1662
IB	−107	0·0660	0·2365	−142	0·0539	0·1661
IIA	−131	0·0870	0·1733	−156	0·0357	0·1311
IIB	−133	−0·0010	0·2064	−156	0·0208	0·1370
IIIA	−146	0·0508	0·1605	−163	0·0239	0·1193
IIIB	−143	0·0351	0·1788	−162	0·0182	0·1188
IVA	139	0·3033	0·5334	−23	ù·3090	0·3349
IVB	122	0·2581	0·5729	−37	0·2591	0·3329
VA	130	0·2196	0·4713	−31	0·2790	0·3340
VIB	80	0·4958	0·4043	−55	0·3329	0·2377

TABLE IV

Chemisorption energies in kJ/mol and the sum of charges on chemisorbed atoms for dissociations displayed in Figs 2 and 3. The first index in this figure corresponds to the position of the C capture and it is the row index in this table

System	Chemisorption energy				Charges			
	I	II	III		I	II	III	
I	−702	−723	−733		−2·4791	−2·5449	−2·5760	
II	−745	−764	−774		−1·8149	−1·9344	−1·9274	
III	−760	−779	−790		−1·8876	−1·9878	−2·0444	
	IVA	IVB	VA	VIB	IVA	IVB	VA	VIB
IVA	−227	−349	−243	−271	−1·0695	−2·4364	−1·1342	−2·1989
IVB	−281	−219	−279	−288	−1·0742	−0·7568	−0·4338	−2·0020
VA	−258	−276	−221	−298	−2·0494	−2·0374	−0·5530	−1·9935
VIB	−311	−326	−323	−310	−1·7848	−1·8601	−1·7853	−1·9769

tion of this fact is that atop adsorption which causes a donation of a CO electron pair to the metal is favored due to the positive charge on the Ir surface. However, the dissociation is caused by the strong electron transfer to both C and O atoms (cf. ref.[3] for the case of Ni), which is evidently not feasible on the positively charged surface. It should be noted that the simpler jellium model (see ref.[19]) exhibits the electron transfer on pure metals from edges to kinks in all cases. Within the view of the MO model the electron transfer is observed in both directions depending on the type of the metal atom and the number of its valence electrons.

CONCLUSION

It can be concluded that atop adsorption will predominate what is in agreement with experimental findings on low index planes[3-10]. Adsorption on atop positions is followed by an electron donation from CO to the metal. The CO bond weakening is 3 to 4 time larger for atop captures than for the n-fold hollow captures. All dissociative chemisorption energies are much less than those for linear captures, thus the dissociative adsorption on this surface seems to be ruled out.

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