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## A TOPOLOGICAL QUANTUM-CHEMICAL STUDY OF THE CHEMISORPTION OF CARBON MONOXIDE ON THE fcc (112) SURFACES OF Ni, Pt, Pd, Rh, and Ir

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A semiempirical quantum-chemical topological method is applied to the study of the fcc (112) surfaces of Ni, Pt, Pd, Rh, and Ir and the nondissociative as well as dissociative chemisorption of carbon monoxide on them. On Ni, dissociative chemisorption is preferred to linear capture, whereas on Pd and Pt, linear capture is preferred although dissociative chemisorption is also feasible. On Rh and, in particular, on Ir, dissociative chemisorption is energetically prohibited. The high dissociative ability of the Ni surface can be ascribed to a rather unusual charge alteration and to the degeneracy of the frontier orbitals. Negative charges at the surface level are only found on the Ni and Pt surfaces whereas concentration of positive charges is established on the Rh and Ir surfaces; the Pd surface is nearly uncharged. Metals with negatively charged surfaces seem to be able to dissociate molecules of carbon monoxide. It is demonstrated that CO adsorption can take place on all metal surface sites, most effectively in the valley of the step. In all the cases studied, the attachment to the surface is found to be energetically more favourable for the carbon than for the oxygen.

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The aim of the present study is to offer an explanation for the different behaviour of Ni, Pt, Pd, Ir, and Rh as fcc transition metals in the process of dissociative or non-dissociative chemisorption of carbon monoxide. Although similar in structure, these metals exhibit rather different behaviour. The calculations performed were based on the quantum-chemical topological method developed by one of us<sup>1</sup>. The same parametrization was applied to all of the metals under study, owing to which the results are at least qualitatively comparable. The chemisorption properties of the metals has been described in detail in refs<sup>2-6</sup>.

Two different types of methods are used for the theoretical description of adsorption processes: methods of solid state physics and methods based on the generalized valence bond (GVB) or the molecular orbital (MO) formalisms. From among methods of the former type, the following have been applied to the adsorption of CO: the EMTO (extended muffin tin orbital) method<sup>7</sup>, the Doyen-Ertl method<sup>8</sup>, the SCF-X $\alpha$ -SW (self-consistent field-X $\alpha$ -scattered wave) methods (see, e.g., ref.<sup>9</sup>), and the tight binding method<sup>10</sup>. From among the "chemical" methods, various versions of

MO methods have been used, from the purely empirical EHT (ref.<sup>11</sup>) and semiempirical CNDO (ref.<sup>12</sup>) and ECNDO (ref.<sup>13</sup>) methods to *ab initio* methods<sup>14</sup>. Some of the work has been done by using the nonempirical GVB methods<sup>15</sup>. Study by any of the methods is, however, very cumbersome and time-consuming because of computational difficulties; even though the orbital basis sets were strongly limited, the calculations were confined to a few metal atoms. Except for the paper<sup>15</sup>, the correlation energy was never considered. The neglecting of the correlation energy at the *ab initio* level is a serious shortcoming, since calculations at the Hartree-Fock level are incapable of reproducing correctly the charge distribution even for CO itself. It is also not yet clear how many atoms have to be taken into account for a correct representation of the metal surface. Estimates exist<sup>16,17</sup> showing that several dozens of metal atoms should be included. Thus, empirical and semiempirical methods continue to be useful provided that they are applied with caution.

### THEORETICAL

In this paper a simple semiempirical topological procedure is used<sup>1</sup> in which the calculation scheme is simplified considerably within the scope of MO methods while retaining at least the qualitative features of the systems, which consist of hundreds of valence electrons. The non-overlaid program occupies 694 Kbytes of inner storage and allows systems involving up to 380 orbitals to be calculated. In our case, the system size was 348 basis orbitals, and a calculation on the IBM 370 Model 148 took about 35 min. This method, which requires only one matrix diagonalization, is thus more than one order of magnitude faster than MINDO-type methods. The use of nonempirical methods is so far impossible for systems of this size. The values of the one-center integrals of the *s*-, *p*-, *d*-, and *f*-type are included in the program for all elements from H to Lw and can be called by simply referring to the atomic symbol. The following approaches were applied: (i) the Born-Oppenheimer and (ii) the valence electrons approximations were adopted; (iii) the basis of equivalent orbitals appropriate to the given structural type was chosen; (iv) the correlation energy and (v) the overlap integrals were neglected; and (vi) the tight binding approximation was adopted. Owing to these approximations, the matrix of Coulomb integrals  $\alpha$  and resonance integrals  $\beta$  was subject to a single diagonalization similar to that in the conventional Hückel<sup>18</sup> and Del Re<sup>19</sup> methods. In contrast to the methods mentioned, the resonance integrals between all pairs of localized orbitals that belong to the nearest neighbour atoms were calculated. Test calculations made at our laboratory gave evidence that the serious shortcomings of the Del Re method that have been pointed at by Hoffmann and Lipscomb<sup>20</sup> are avoided here. Moreover, the most important shortcoming of all one-electron methods, including the extended Hückel method, viz. the overestimation of the charge distribution on polar bonds, is eliminated by the appropriate scaling of the Coulomb integrals described below.

The values of the Coulomb integrals  $\alpha$  of canonical orbitals were set equal to the negative Mulliken orbital electronegativities, which were scaled similarly to the approach in ref.<sup>2</sup>. The values used for the present study are given in Table I.

The radial parts of the resonance integrals  $\beta$  for the Me—Me and Me—O bonds were calibrated on the experimentally found heats of formation for diatomic molecules. For the Me—C(O) and (Me)C—O bonds, the bonding energies of metal carbonyls<sup>21</sup> and CO<sub>2</sub> (ref.<sup>22</sup>) were used, because these bonds can be regarded as similar to those in the systems under study<sup>23</sup>. The values used in this study are given in Table II; the  $\beta$ -integrals for the C—O bonds in the adsorbed molecule and in the isolated molecule,  $-103$  kJ/mol (taken from CO<sub>2</sub>) and  $-121$  kJ/mol (taken from CO), respectively, were adopted for all the systems.

TABLE I

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

Element	(s)	(p)	(d)	(f)
Ni	-715	-372	-1 029	0
Pd	-393	-195	-826	0
Pt	-382	-125	-866	0
Ir	-655	-251	-872	0
Rh	-505	-274	-789	0
C	-1 473	-597	0	0
O	-2 507	-991	0	0

TABLE II

Resonance integrals  $\beta$  in kJ/mol for the top and  $n$ -fold hollow captures of the CO molecule on metal surfaces

Metal	Top			$n$ -Fold hollow	
	$\beta(\text{Me-Me})$	$\beta(\text{Me-C})$	$\beta(\text{Me-O})$	$\beta(\text{Me-C})$	$\beta(\text{Me-O})$
Ni	-132	-103	-106	-65	-67
Pt	-172	-113	-100	-22	-19
Pd	-80	-103	-45	-50	-37
Ir	-132	-103	-83	-23	-18
Rh	-104	-105	-69	-37	-25

When treating the resonance integrals of the metal adsorbate in the bridge and hollow positions, the bond lengths were assumed to be close to those of the Me—Me bonds<sup>24</sup>. The energy reduction was obtained by using the Morse function based on experimental data. The values of the resonance integrals for these multiple positions are summarized in Table II.

The (112) plane of the fcc surfaces was subject to investigation; this plane was chosen with regard to the fact that this is the only low-index plane which exhibits steps. From experimental work it is well known that dissociation of carbon monoxide takes place particularly on step and kink sites<sup>25–28</sup>.

The structure of the fcc (112) surface is shown in Fig. 1. The plane consists of terraces constituted by the (111) subplane and of steps constituted by (100) subplanes; hence, it can be said that the (112) plane is composed of (111) and (100) strips. Atoms shown as full squares in the figure constitute the basic structural unit which is actually used in the calculations. The semi-infinite metal crystal is modelled by using periodic boundary conditions. The leftmost atoms in the elementary unit were linked to the rightmost atoms by formal chemical bonds, and the foremost atoms of the basic structural unit were similarly linked to the atoms in the rear.

The torus represents an infinite crystal with nine elementary (112) planes. Owing to the conservation of translational symmetry, atoms in the corresponding planes are identical and the torus as a whole has degenerate frontier orbitals. The high reactivity

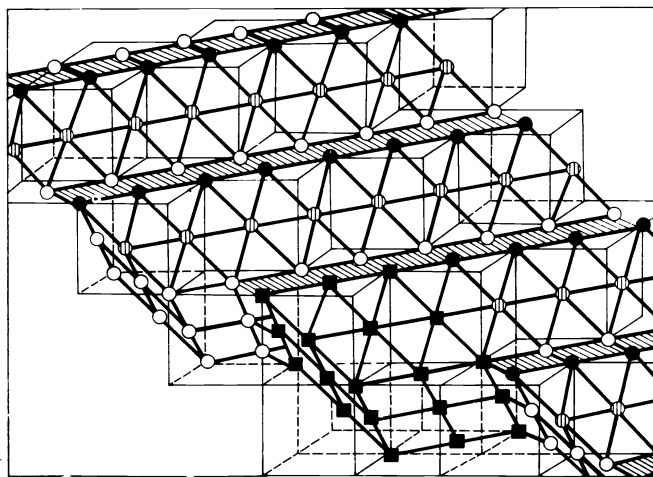


FIG. 1

The (112) plane of the fcc crystal. Atoms which constitute the basic structural unit are designated by full squares

of this stepped surface can be easily understood in terms of the frontier orbital theory (see e.g.<sup>29</sup>).

It is noteworthy that only atoms of the three layers nearest to the surface bear equivalent orbitals, the atoms in the respective layers being identical. Thus, three types of on top trapping can be identified. Moreover, as Fig. 2 demonstrates, equivalent free orbitals of these atoms intersect at three distinct positions only (open circles in Fig. 2). These three types can be identified with the directions of crystal growth. It can be expected that such positions will also play an important role in the trapping of molecules. Adsorbed on these molecules, a molecule is joined to two, three or five nearest neighbouring metal atoms; these centers can be identified with bridge, three-fold and five-fold hollow centers, respectively. In this manner, our discussion is limited to six trapping centers, denoted as I–VI in the tables.

The influence of the bond angle between the molecule and the metal surface and of the bond energy is studied for two typical angles only, viz. for the CO molecule bonded perpendicularly either to the terrace (111) plane (denoted as A position in the tables) or to the step (100) plane (denoted as B position). Considering the inter-

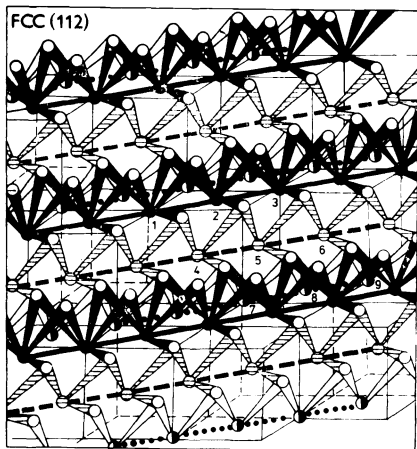


FIG. 2  
Directions of equivalent orbitals on the (112) surfaces of the fcc crystals

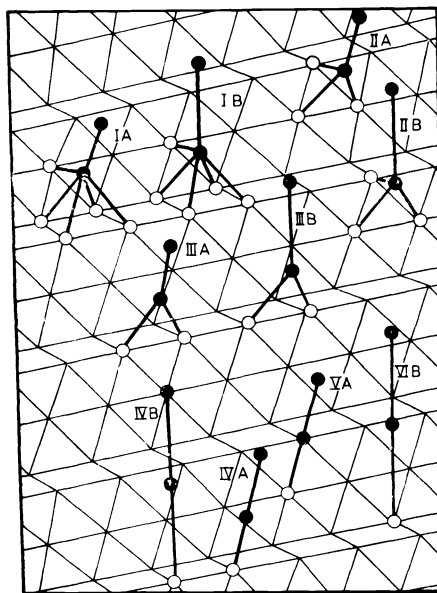


FIG. 3  
Linear CO captures studied in this work

action of the metal either with carbon or with oxygen, we have 20 typical positions for adsorption; they are shown in Fig. 3. All the dissociation positions studied are shown in Figs 4 and 5.

## RESULTS AND DISCUSSION

The calculated charge densities for all the metals studied and for the various planes are given in Table III. Negative charges on the surface layer were only found for the Ni and Pt surfaces, whereas positive charges are concentrated on Rh and Ir surfaces; the Pd surface is nearly uncharged. Positively charged surfaces are typical of metals with lower numbers of *d*-electrons. The addition of the 8th *d*-electron results in an increase in the electronic repulsion, and electrons are displaced towards the outer crystal layers. The lower charge alteration in Pd can be explained in terms of its extremely low bond strength,  $-80 \text{ kJ mol}^{-1}$ , as compared with the values of  $-132$  and  $-172 \text{ kJ mol}^{-1}$  for Ni and Pt; this brings about a considerable independence of the atoms in this crystal.

The bond orders on the subsequent planes are given in Table IV for all the metals studied. They are tabulated for those atoms only which are in the same plane. The

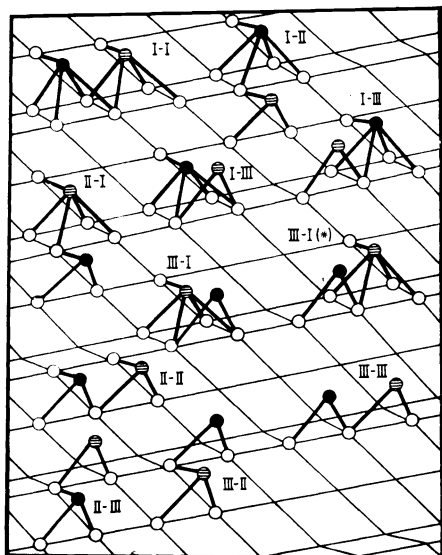


FIG. 4

Dissociative CO captures between *n*-fold hollow centers studied in this work

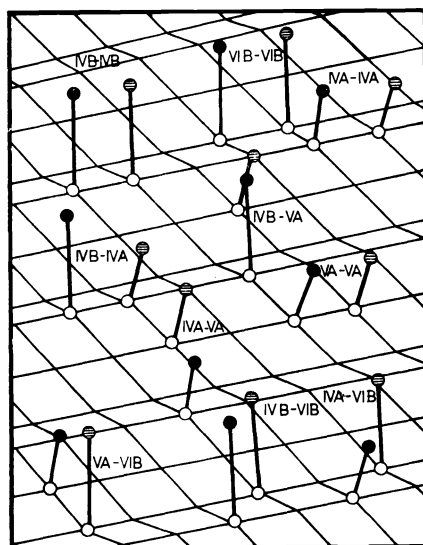


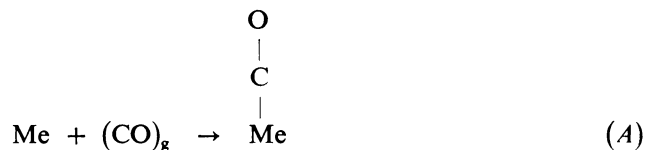
FIG. 5

Dissociative CO captures on top centers studied in this work

capture of CO via its oxygen is energetically less favourable than via its carbon; this applies to all cases on all metal surfaces<sup>2-6</sup>. Therefore, only the capture of carbon monoxide via its carbon will be discussed in this paper.

### *Nondissociative Chemisorption*

The energies of the nondissociative chemisorption



are summarized in Table V for all the metals under study.

TABLE III

Charge densities on the subsequent planes of the (112) crystals, consisting of 9 layers

Metal	Surface layers			Bulk	
	1	2	3	4	5
Ni	-0.38	0.21	0.01	0.01	0.33
Pt	-0.56	0.22	0.13	0.11	0.22
Pd	-0.00	0.15	-0.02	-0.11	-0.00
Rh	0.13	0.22	-0.25	-0.11	0.07
Ir	0.22	0.07	-0.16	-0.12	0.03

TABLE IV

Bond orders on the subsequent planes of the (112) crystals consisting of 9 layers

Metal	Surface layers			Bulk	
	1	2	3	4	5
Ni	1.13	0.76	0.63	0.54	0.57
Pt	1.22	0.92	0.73	0.66	0.65
Pd	1.08	0.74	0.68	0.10	0.57
Rh	1.12	0.81	0.71	0.64	0.07
Ir	1.36	0.85	0.78	0.67	0.75

The stability on the Ni crystal decreases in order  $I \gg II > IV > V > VI > III$ . The exceedingly high adsorption energy in the five-fold hollow position suggests that the molecule is preferentially captured at the ledge sites. Noticeable, on the other hand, is the very low adsorption energy in the bridge position.

On platinum, the stability of the adsorbate complex decreases in order  $IV > V > VI \gg I > II > III$ . The high adsorption energy in the top positions suggests that the molecule is captured preferentially at the top sites. Noticeable is the very low adsorption energy in the multiple positions.

The stability of the adsorbed complexes on palladium decreases in order  $I > V \approx IV > VI > II > III$ . The energy gain in the 5-fold hollow positions is higher than in the top positions and substantially higher than in the 3-fold and 2-fold hollow positions; this suggests that the molecule is preferentially captured at the ledge sites. The difference between the adsorption energies in the top positions and the 5-fold hollow positions, however, is not so high as on the nickel surfaces.

On iridium the stability of the adsorbed complexes decreases in order  $IV > V > VI \gg I > III$ . The energy gain in the top positions is remarkably high (higher than in the multiple positions) and suggests preferential capture of the molecule at the ledge sites. The very low adsorption energy in the bridge position, on the other hand, is noticeable.

The stability of the adsorbed complex on rhodium decreases in order  $IV > V > VI > I > II > III$ . The energy gain in the 5-fold hollow position is lower than in any other position. The exceedingly high adsorption energy in all top positions

TABLE V

Energy of nondissociative chemisorption in kJ/mol for all the systems under study (shown in Fig. 6)

System	Metal				
	Ni	Pt	Pd	Ir	Rh
<i>IA</i>	310	-125	197	-107	29
<i>IB</i>	311	-126	161	-107	29
<i>IIA</i>	148	-150	89	-131	-46
<i>IIB</i>	137	-144	89	-133	-45
<i>IIIA</i>	49	-154	12	-146	-85
<i>IIIB</i>	56	-153	14	-143	-80
<i>IVA</i>	123	183	178	139	168
<i>IVB</i>	87	149	139	123	132
<i>VA</i>	117	178	180	130	157
<i>VIB</i>	72	118	138	89	114



suggests that the molecules are captured preferentially at them. Worth mention is the very low adsorption energy in position *III*.

In conclusion, multiple captures of the molecule are preferred on nickel and palladium, whereas top captures are preferred on iridium, rhodium and platinum (Table VI). This is in agreement with the results obtained previously<sup>2-6</sup>.

The total amounts of charge on carbon monoxide are summarized in Table VII. The electron pair at the carbon atom is seen to have an electron donation effect, which is important in the top positions. The  $\pi$ -electrons at the CO bond have a back-donation effect, prevailing in the bridge and/or hollow positions. The higher the adsorption

TABLE VI

Preferential positions of the CO capture in the nondissociative chemisorption processes

Metal	Capture position
Ni	<i>n</i> -fold hollow $\neq$ top
Pt	<i>n</i> -fold hollow $\neq$ top
Pd	<i>n</i> -fold hollow $<$ top
Ir	top
Rh	top

TABLE VII

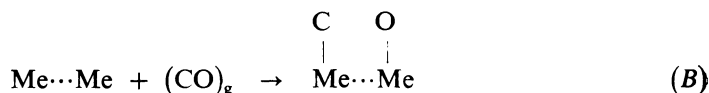
Total amounts of charge *Q* on the adsorbed molecules for all the systems under study (shown in Fig. 3)

System	Metal				
	Ni	Pt	Pd	Ir	Rh
<i>IA</i>	-0.103	-1.659	-1.192	0.066	-0.595
<i>IB</i>	-0.123	-1.658	-2.586	0.066	-0.595
<i>IIA</i>	0.171	-0.854	-0.851	0.087	-0.223
<i>IIB</i>	0.027	-1.258	-1.005	-0.001	-0.427
<i>IIIA</i>	0.064	-0.809	-1.089	0.051	-0.225
<i>IIIB</i>	0.030	-0.649	-1.724	0.035	-0.255
<i>IVA</i>	0.338	-1.349	-0.513	0.303	-0.234
<i>IVB</i>	0.388	-0.327	-0.707	0.258	-0.249
<i>VA</i>	0.398	-1.337	-0.380	0.219	-0.084
<i>VIB</i>	0.372	-1.353	-0.390	0.496	-0.017

energy, the weaker the CO bond (Tables V and VIII); this is also confirmed experimentally.

### *Dissociative Chemisorption*

The energies of the dissociative chemisorption (energy gain) of CO and the sums of charges  $Q$  on the chemisorbed atoms in the process



are given in Table IX.

Dissociative chemisorption on nickel can only occur between a 5-fold hollow position and a 5-fold, 3-fold or 2-fold position. The chemisorption energy between two 5-fold hollow positions is exceedingly high, suggesting thus preferential cleavage of the CO bond between 5-fold hollow centres of capture. Noticeable, on the other hand, is the very low (negative) chemisorption energy for 3-fold or 2-fold hollow captures. This suggests that the 5-fold hollow centres, and the ledge sites, play a major role in the cleavage of the CO bond.

The results for the platinum surface (Table IX) indicate that dissociative chemisorption of the adsorbed complex can only occur between top positions. An exceptionally high chemisorption energy was found between the  $VA$  and  $VA$  top positions; the energy gain for the nondissociative capture in these positions, however, is about  $78 \text{ kJ mol}^{-1}$  higher.

On palladium, dissociative chemisorption can only occur between the 5-fold hollow positions; the  $E_b$  for the linear capture on them, however, is about  $170 \text{ kJ mol}^{-1}$  higher, so that nondissociative chemisorption is preferred. On the rhodium surface, dissociative chemisorption is energetically prohibited, and on the iridium surface it is energetically highly unfavourable ( $-700 \text{ kJ mol}^{-1}$ ).

In conclusion, dissociative chemisorption is energetically prohibited on rhodium and, in particular, on iridium surfaces, whereas on nickel it is preferred. On plaladium and platinum, dissociative chemisorption is energetically feasible, linear capture, however, is more favourable (Table X).

### CONCLUSION

A semiempirical quantum-chemical topological method was applied to the study of the fcc (112) surfaces of Ni, Pd, Pt, Rh, and Ir and the nondissociative as well as dissociative chemisorption of carbon monoxide on them. On platinum and iridium, linear capture predominates over the dissociative chemisorption, whereas the reverse is true of the nickel surface. Dissociative chemisorption is energetically prohibited on

TABLE VIII  
Relative bond order changes  $-\Delta p$  on CO bonds for all the metals under study (shown in Fig. 3)

System	Metal				
	Ni	Pd	Ir	Rh	Pt
<i>IA</i>	0.964	1.428	0.2365	0.920	1.261
<i>IB</i>	0.964	1.743	0.2365	0.920	1.260
<i>IIA</i>	0.602	1.157	0.1733	0.570	0.735
<i>IIB</i>	0.686	1.185	0.2066	0.685	1.023
<i>IIIA</i>	0.584	0.981	0.1605	0.508	0.721
<i>IIIB</i>	0.599	0.986	0.1788	0.528	0.629
<i>IVA</i>	0.507	1.072	0.5334	0.890	1.436
<i>IVB</i>	0.524	1.158	0.5729	0.895	1.434
<i>VA</i>	0.417	0.979	0.4713	0.761	1.404
<i>VIB</i>	0.398	0.958	0.4043	0.690	0.375

TABLE IX

Chemisorption energies in kJ/mol and the sums of charges  $Q$  on the chemisorbed atoms for dissociations displayed in Figs 4 and 5 (the row indices in this figure correspond to the position of the C capture and the column indices in the heading correspond to the O capture)

Metal	System	Chemisorption energy			$Q$		
		<i>I</i>	<i>II</i>	<i>III</i>	<i>I</i>	<i>II</i>	<i>III</i>
Ni	<i>I</i>	346	169	23	-1.126	-1.373	-1.731
	<i>II</i>	122	-53	-202	-1.373	-1.906	-2.015
	<i>III</i>	10	-170	-302	-0.565	-1.051	-1.239
Pt	<i>I</i>	-398	-407	-412	-5.703	-5.723	-5.736
	<i>II</i>	-413	-426	-425	-5.796	-5.816	-5.832
	<i>III</i>	-425	-431	-438	-5.949	-5.870	-5.888
Pd	<i>I</i>	30	-29	-67	-3.292	-3.493	-3.652
	<i>II</i>	-127	-191	-232	-3.646	-3.825	-3.967
	<i>III</i>	-229	-294	-327	-3.863	-4.025	-4.163
Ir	<i>I</i>	-702	-723	-733	-2.479	-2.545	-2.576
	<i>II</i>	-745	-764	-774	-1.815	-1.934	-1.927
	<i>III</i>	-761	-779	-790	-1.843	-1.9878	-2.044
Rh	<i>I</i>	-341	-370	-388	-3.845	-3.972	-4.033
	<i>II</i>	-437	-466	-485	-4.182	-4.274	-4.346
	<i>III</i>	-498	-526	-547	-4.228	-4.325	-4.414

TABLE IX (Continued)

Metal System	Chemisorption energy				Q				
	IVA	IVB	VA	VIB	IVA	IVB	VA	VIB	
Ni	IVA	-165	-131	-201	-245	-1.306	-1.586	-1.243	-1.224
	IVB	-192	-219	-470	-244	-1.611	-1.197	-1.486	-1.224
	VA	-184	-398	-153	-236	-1.155	-1.132	-0.745	-1.524
	VIB	-261	-261	-215	-246	-1.189	-1.189	-1.194	-0.685
Pt	IVA	49	26	31	0	-4.953	-3.944	-4.018	-4.094
	IVB	-264	-1	6	1	-5.186	-3.933	-4.004	-4.094
	VA	45	17	100	2	-4.126	-4.199	-4.279	-4.303
	VIB	-257	-4	-3	-2	-4.209	-4.271	-4.273	-4.525
Pd	IVA	-62	-412	-68	-87	-3.435	-4.633	-3.531	-3.499
	IVB	-409	-132	-108	-395	-4.781	-3.357	-3.454	-4.512
	VA	-124	-112	-51	-106	-3.341	-3.385	-3.851	-3.435
	VIB	-145	-146	-123	-108	-3.528	-3.528	-3.451	-3.502
Ir	IVA	-227	-349	-243	-271	-1.070	-2.436	-1.134	-2.199
	IVB	-281	-219	-279	-288	-1.0742	-0.757	-0.434	-2.002
	VA	-258	-276	-221	-298	-2.049	-2.0374	-0.553	-2.194
	VIB	-311	-326	-323	-310	-1.785	-1.860	-1.785	-1.972
Rh	IVA	-136	-163	-146	-249	-3.206	-3.146	-3.2018	-3.600
	IVB	-510	-202	-185	-205	-4.518	-3.129	-3.3611	-3.445
	VA	-161	-180	-126	-183	-3.354	-3.3586	-3.615	-3.423
	VIB	-355	-229	-211	-199	-3.386	-3.444	-3.504	-3.808

TABLE X  
The preferential types of capture of CO molecule on the metal surfaces

Metal	Capture type
Ni	dissociative $\geq$ nondissociative
Pt	dissociative $<$ nondissociative
Pd	dissociative $<$ nondissociative
Rh	nondissociative
Ir	nondissociative

rhodium and, in particular, on iridium. Negative charges on the surface level were only found for nickel and platinum, whereas positive charges were found to be concentrated on the surfaces of rhodium and iridium. Palladium surface is nearly un-

charged. The metals with negatively charged surfaces seem to be able to dissociate the molecule of carbon monoxide. The absorption of CO can take place on all metal surface sites, most effectively in the valley of the step.

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