

Adsorption and dissociation of CO on Ni (III), an extended Hückel molecular orbital investigation

Citation for published version (APA):

van Langeveld, D., Koster, de, A., & Santen, van, R. A. (1990). Adsorption and dissociation of CO on Ni (III), an extended Hückel molecular orbital investigation. *Surface Science*, 225(1-2), 143-150.
[https://doi.org/10.1016/0039-6028\(90\)90432-8](https://doi.org/10.1016/0039-6028(90)90432-8)

DOI:

[10.1016/0039-6028\(90\)90432-8](https://doi.org/10.1016/0039-6028(90)90432-8)

Document status and date:

Published: 01/01/1990

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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ADSORPTION AND DISSOCIATION OF CO ON Ni(111) AND STEPPED Ni(111); AN EXTENDED HUCKEL MOLECULAR ORBITAL INVESTIGATION

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Received 21 June 1989; accepted for publication 4 September 1989.

The atom superposition and electron delocalization molecular orbital (ASED-MO) method has been used to describe the adsorption of C, O and CO on a Ni(111) surface. Various reaction paths for CO dissociation have been investigated, resulting in a mechanism with an activation energy nearly equal to the adsorption energy.

The influence of a monoatomic step with (110) geometry on the heat of adsorption, the structure of the adsorbate substrate complex, and the activation energy of CO dissociation has been investigated. The results suggest that a new type of chemisorption complex can be formed of which the activation energy for dissociation is 34% lower than on the (111) plane. The heat of adsorption of this complex is almost equal to that on the Ni(111) terrace.

1. Introduction

Catalytic reactions of small molecules play an important role in various applications of economic and environmental importance. Although an enormous progress has been made from experimental point of view in the last decades, a fundamental (theoretical) understanding on the molecular scale of most processes is still missing.

A challenging system to investigate from a theoretical point of view is the adsorption and dissociation of CO on Ni. Because of the importance of Ni as a methanation catalyst, the system has been well characterized by various modern surface sensitive techniques. From these results, it follows that the most densely packed surfaces of Ni have only a low activity in the dissociation of CO, whereas defect structures and steps seem to have a high activity.

The applicability of the atom superposition and electron delocalization molecular orbital (ASED-

MO) method [1–15] on the surface chemistry of this system has been tested. In this method both attractive and repulsive interactions are accounted for. The Ni cluster used in the calculations consisted of 29 atoms distributed over two layers with (111) geometry. The size and dimensions of the cluster were chosen in such a way that effects due to the presence of edges were reduced to second order effects. In case of the stepped (111) surface, 6 additional atoms were placed on the cluster simulating the (111) surface. A schematic representation of the cluster containing 35 atoms is shown in fig. 1.

2. Results and discussion

2.1. Adsorption of C, O and CO on Ni(111)

First, the adsorption energies of C, O and CO have been calculated to estimate the heat of the dissociation reaction. Furthermore, the local density of states (LDOS) of CO on the various types of sites has been calculated to reveal additional differences.

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Table 1
The atomic parameters used in the calculations

Atom	Shell											
	s			p			d					
	<i>n</i>	VSIP	ζ	<i>n</i>	VSIP	ζ	<i>n</i>	VSIP	ζ	C_1	C_2	ζ_2
Ni	4	7.8	2.10	4	3.7	2.10	3	9.9	5.75	0.5683	0.6292	2.0
C	2	18.2	1.63	2	9.5	1.63						
O	2	29.6	2.27	2	12.0	2.27						

The adsorption energy was calculated by minimizing the total energy of the cluster in varying the height Z of the adsorbate above the metallic surface. The atomic parameters used have been published previously by Sung and Hoffmann [16]. In case of O, the large difference in electron affinity with the metallic cluster caused an electron transfer with a corresponding energy gain at larger distances. As a consequence, no minimum

was present in the $E(Z)$ curve. To circumvent this problem, the inner potential of the O2p level was decreased until a minimum in the $E(Z)$ curve could be observed. This inner potential (-12.00 eV) has been used throughout all calculations. All parameters are collected in table 1.

For gasphase CO, the total binding energy is -6.70 eV at an equilibrium distance of 1.15 Å. These values are in good agreement with data presented by Herzberg [17]; the interatomic distance is only 2% too large, while the total binding energy is 40% too low. The latter, however, is the result of the adjustment of the O2p inner potential.

In table 2, the following results are presented: the adsorption energy (total energy, including both repulsive and attractive interactions), $E_{\text{ads}}^{\text{tot}}$, the height Z of the adsorbate above the surface, and the adsorbate-nearest metallic neighbour dis-

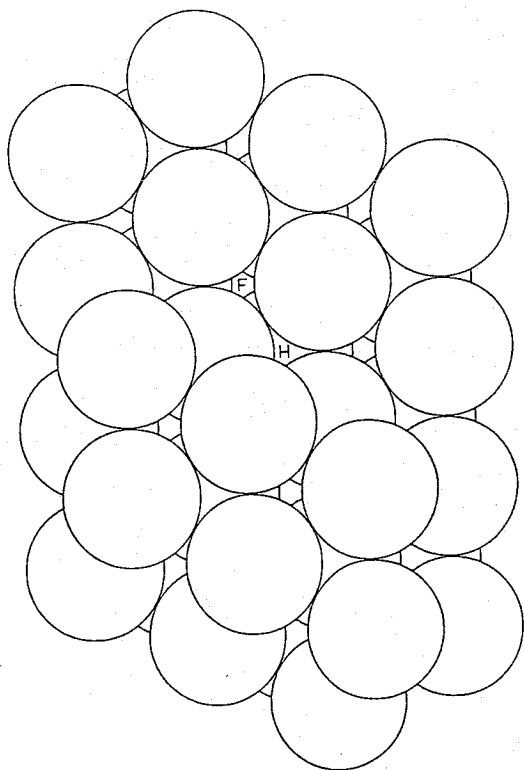


Fig. 1. A topview of the Ni-35 cluster, including the 6 step atoms. The fcc and hcp site next to the step are indicated by an F and an H, respectively.

Table 2
Properties of C, O and CO adsorbed on Ni(111)

Species	Site	$E_{\text{ads}}^{\text{tot}}$ (eV)	Z (Å)	D (Å)
C	1-fold	3.20	1.80	1.80
	2-fold	3.62	1.45	1.91
	3-fold fcc	3.82	1.40	2.00
	3-fold hcp	3.94	1.35	1.97
O				
O	1-fold	5.36	1.40	1.40
	2-fold	4.87	0.80	1.48
	3-fold fcc	5.17	0.50	1.52
	3-fold hcp	5.10	0.50	1.52
CO	1-fold	1.16	1.80	1.80
	2-fold	1.56	1.45	1.91
	3-fold fcc	1.58	1.30	1.94
	3-fold hcp	1.70	1.35	1.97

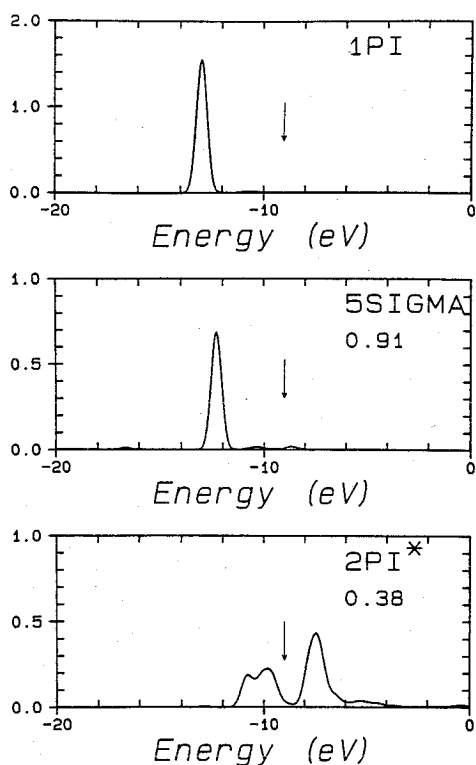


Fig. 2. The local density of states of the 1π , 5σ , and $2\pi^*$ levels of the fcc site chemisorbed CO. The numbers in the figures are the orbital populations of the respective orbitals; the position of the Fermi-level (at -8.9 eV) is indicated by an arrow.

tance, D . The surface is defined as the plane through the nuclei of the outermost layer of the Ni atoms. The accuracy in $E_{\text{ads}}^{\text{tot}}$ on one type of site is about 0.1 eV, since $E_{\text{ads}}^{\text{tot}}$ depends on the position of the site in the cluster, and on the geometry of the metallic cluster.

For CO, the most stable adsorption site is the three-fold position. From energetic point of view the fcc and hcp sites on the cluster are identical; a change in the position of the atoms in the subsurface layer modified an fcc site into an hcp and vice versa. Notwithstanding that, the adsorption energy did not vary. The increasing adsorption energy with increasing coordination number of CO is in accord with results presented in the literature [18–24]. The total adsorption energy values are in good agreement with data of Shustorovich and Bell [25], Kristman et al. [26], Bullet and Cohen [27], Gijzeman et al. [28] and of Frank et al. [29]. The Ni–C bond length is in reasonable agreement with data of Brockway et al. [30] and of Hannaman et al. [31].

The local density of states, $\rho_i(E)$ of fcc adsorbed CO is shown in fig. 2. It has been calculated using the following equation:

$$\rho_i(E) = \sum_k |\langle \psi_i | \phi_k \rangle|^2 \delta(E - E_k), \quad (1)$$

ψ_i being the molecular orbital fragment (of CO)

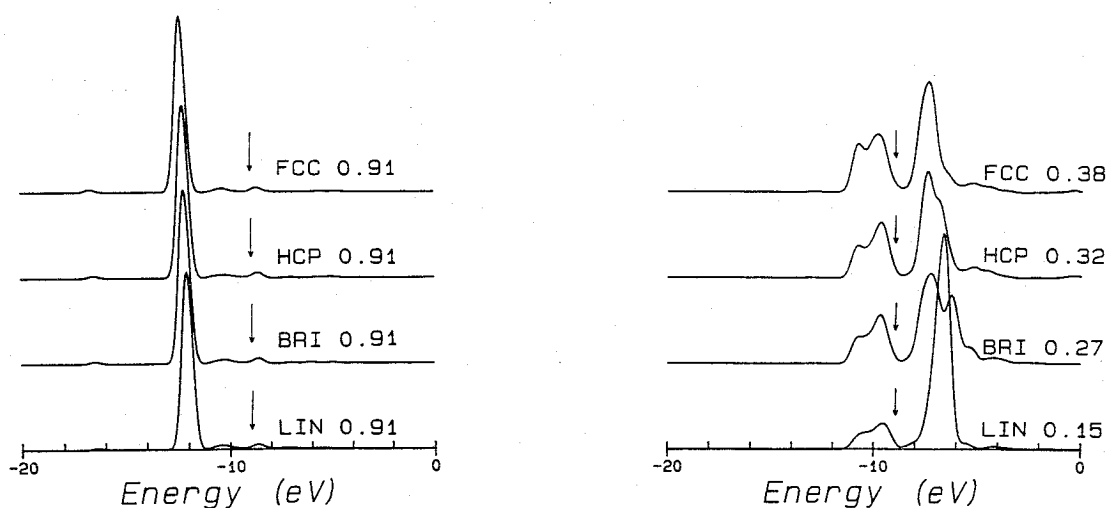


Fig. 3. The local density of states of (a) the 5σ and (b) the $2\pi^*$ levels for the various types of CO chemisorbed on Ni(111); the orbital populations are indicated by the numbers in the figures. The position of the Fermi-level at -8.9 eV is indicated by an arrow.

for which the LDOS is calculated, and ϕ_k being the molecular orbital (of energy E_k) of the system as a whole (CO and the metallic cluster). This expression has been smoothed with a Gaussian function of 0.25 eV in width. The orbital population (the numbers at the various curves in the figures) P_i are given by:

$$P_i = \int_{-\infty}^{E_F} \rho_i(E) dE. \quad (2)$$

Present results indicate the 1π level to be at -0.4 eV with respect to the 5σ level, in contrast with experimental data of Williams et al. [32]. The discrepancy may be due to differences in the screening effect of the final state which effect is not accounted for in the ASED method. In fig. 3 the LDOS of the 5σ and $2\pi^*$ levels are shown in more detail. Going from one-fold to three-fold fcc adsorbed CO, the position of the maximum of the 5σ level shifts by about -0.3 eV, and the unfilled $2\pi^*$ levels also shift to higher binding energy. In the same sequence, the amount of $2\pi^*$ backdonation increases from 14% to 36%, in accord with results of vibrational spectroscopies [18–24]. The position of the maximum of the unfilled $2\pi^*$ level of the fcc and hcp site chemisorbed CO at 1.7–1.8 eV with respect to the Fermi level is in accord with results of inverse photoemission experiments of Frank et al. [29].

Based on the total energy, C prefers the highest coordination number; the difference between the fcc and hcp site is caused by the geometric effect. Comparison with data of Frese [33], Shustorovitch and Bell [25] and of Shustorovitch [34] indicates that adsorption energy may be 50% too low.

For O, the most stable adsorption site is atop, however, the difference with the three-fold site is rather limited. High energy ion scattering experiments of Narusawa et al. [35] and LEED experiments of Marcus et al. [36] indicate O to adsorb preferentially in three-fold sites. The Ni–O bond length is in accord with results of Marcus et al. [36] and of Walch and Goddard [37]. The total adsorption energy is in general agreement with theoretical results of Shustorovitch and Bell [25] Frese [33], and experimental results of Pankratjev et al. [38], Horgan and King [39] and Sakumbajeva et al. [40].

Based on the adsorption energies of C, O and CO on their most stable positions we calculate the dissociation reaction to be exothermic by 0.9 eV.

In conclusion, the three-fold fcc and hcp adsorbed CO are most strongly bound to the Ni(111) surface. Of these, the fcc type has a higher degree of $2\pi^*$ backdonation. Consequently, we expect this type of chemisorbed CO to be the precursor for the dissociation reaction.

2.2. Dissociation of CO on Ni(111)

Dissociation of CO has been investigated starting from fcc site chemisorbed CO. In order to reduce the problem of the possible reaction paths, an energy mapping procedure was developed. A plane perpendicular to the surface, containing the nuclei of the CO molecule and one of the contiguous Ni atoms has been created. In this plane, a two-dimensional energy map as a function of the coordinates of the O atom has been calculated. From it, the reaction path has been acquired in search for the smallest increase of the total energy content while moving the O away from the C. In table 3 all details of relevance, the change in total energy with respect to the equilibrium position, ΔE^{tot} , the C–O distance D , the height Z of the O atom above the metallic surface and its lateral displacement L , are collected.

Table 3
Dissociation of fcc adsorbed CO on Ni(111)

ΔE^{tot} (eV)	D (Å)	Z (Å)	L (Å)	
0.00	1.20	2.50	0.00	
0.04	1.22	2.50	0.20	
0.18	1.26	2.50	0.40	
0.29	1.17	2.30	0.60	
0.67	1.13	2.10	0.80	
0.78	1.17	1.90	1.00	
1.00	1.26	1.70	1.20	
1.54	1.41	1.50	1.40	O atop
1.69	1.61	1.50	1.60	
1.52	1.80	1.40	1.80	
1.07	2.00	1.30	2.00	
0.57	2.20	1.20	2.20	
0.24	2.41	1.10	2.40	
-0.02	2.63	0.90	2.60	

In the reaction path with the lowest activation energy, the CO molecule first tilts towards one of the adjacent Ni atoms, followed by a CO bond stretch; this stretch causes a large increase in energy of the system. Subsequently, the O passes through the one-fold chemisorption site of "pure" O, and then moves straight on towards the hcp site. The total activation energy of this process is 1.69 eV, the adsorption energy being -1.58 eV. The same activation energy is found on another cluster, there the adsorption energy equals -1.70 eV. This reaction mechanism has been calculated through starting from various fcc sites. The activation energy is always within 0.05 eV equal to 1.69 eV.

In conclusion, the activation energy for CO dissociation on Ni(111) is almost equal to the heat of adsorption of CO.

2.3. The influence of a step on the heat of adsorption and the activation energy for dissociation of CO

As a first approximation the CO molecules have been placed on an fcc and an hcp site in the proximity of the step perpendicular to the (111) terrace, see fig. 1. Starting from these adsorption complexes no reaction path for CO dissociation has been found with an activation energy lower than on the Ni(111) surface. In addition, the adsorption energies were significantly lower than on the (111) surface due to a strong repulsive interaction between the Ni step atoms and the CO molecule. Since, however, a step has a geometrical structure [41], its presence will not only affect the energy content, but also the structure of the adsorbate complex. Consequently, both the fcc and hcp chemisorbed CO have been relaxed by optimization of the C and the O coordinates with a resolution of 0.02 Å. An investigation of the cluster shown in fig. 1 will reveal that the step under investigation has an (110) structure.

The result of the hcp site chemisorbed CO is shown in fig. 4 as a sideview cross-section. In this cross-section, the (111) and (110) planes are indicated as lines. Clearly, the C of the CO is coordinated by the two protruding Ni atoms in the plane of the figure (drawn in fat circles). The Ni-C and C-O interatomic distances are equal to that of the

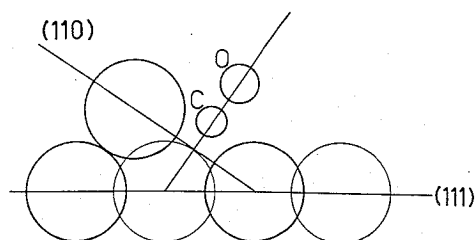


Fig. 4. A cross-section sideview of two-fold ("relaxed hcp site") chemisorbed CO over the valley of the (110) structure. The largest circles represent Ni atoms. The atoms drawn in fat lines are in the plane of the cross-section, while those with a thin line are projections of atoms in front of and behind the plane of the cross-section. The (111) and (110) crystallographic planes (perpendicular to the cross-section) are indicated by lines.

two-fold chemisorbed CO on Ni(111). The adsorption energy of this complex is -1.48 eV, almost equal to that of two-fold chemisorbed CO on Ni(111), see table 2. The original adsorption energy on the hcp site is -1.70 eV. The $2\pi^*$ level of this complex is filled for 31%, only slightly higher than the hcp complex on Ni(111). Starting from this complex, no reaction path for CO dissociation has been found with an activation energy lower than on the Ni(111) surface.

In fig. 5 the results of the fcc site chemisorbed CO are presented. Two stable configurations have been found, of which the total adsorption energy differed by 0.02 eV. In the first configuration, the C on the terrace (marked with "t" in the figure) is displaced 0.1 Å away from the step, while its height is increased by 0.1 Å. The CO distance equals 1.2 Å, and, as a result of repulsion between the doubly occupied 1π orbital of the CO molecule and the Ni step atoms [42], the CO axis was bent for 13° with respect to the normal of the (111) surface. In this position, the O is nearly equally coordinated by all four protruding Ni atoms. The total adsorption energy of this complex is -1.44 eV, only 0.14 eV less than the undisturbed fcc complex on this site of the (111) surface. In the second configuration, the C atom is positioned in the proximity of the fcc site in the step (indicated with "s" in the figure); the adsorption energy of this complex is -1.46 eV.

At larger distances from the step all adsorption energies decreased by 0.1–0.13 eV upon the intro-

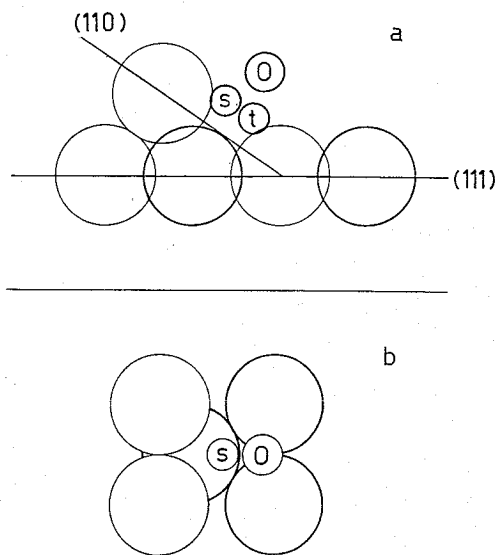


Fig. 5. (a) A cross-section sideview of the two relaxed configurations of fcc site chemisorbed CO, and (b) a top view of the relaxed fcc chemisorbed CO of which the carbon is coordinated with the Ni step atoms. The step and terrace site adsorbed C of the CO are indicated by "s" and "t", respectively.

duction of the step (the geometric effect). Consequently, we conclude that the adsorption energy of the relaxed fcc complexes is almost equal to that of CO adsorbed on the (111) terrace. In the present calculations electrostatic dipole effects of a step are not accounted for. As a result, the calculated adsorption energies may be too low by at most 0.01 eV [30]. Of both complexes the $2\pi^*$ level is filled for 30%, less than for the fcc site chemisorbed CO on the terrace. As a result, the infrared absorption frequency of this complex will be shifted to higher frequencies, in disagreement with results of Erley et al. [43].

The tilt of the CO molecule is in accord with results of Tamaru et al. [44] on a stepped Ru(0001) surface, and in quantitative agreement with results of Somers et al. [45] on a Pt(533) surface. The structure of these fcc site chemisorbed complexes is in general agreement with results of Hannaman and Passler [31] for CO chemisorbed on Ni(110). Differences may be caused by repulsive interactions in the adsorbate layer under the experimental conditions used by Hannaman and Passler. These intermolecular repulsive interactions are not

accounted for in the present calculations, since we minimized the energy content of the system for one single CO molecule on the surface of the cluster. Also, the adsorption energy of these complexes is in quantitative agreement with results of Bauhofer et al. [46] on Ni[110] ($E_{\text{ads}} \approx -1.40$ eV for $\theta \approx 1$).

In the dissociation of the first complex (C marked with "t"), the CO molecule initially tilts towards one of the adjacent Ni step atoms, followed by a CO stretch. The activation energy for this reaction is 1.40 eV, lower than on the (111) terrace, but almost equal to the heat of adsorption of this complex (1.44 eV). For the dissociation of the second complex (C marked with "s"), the most favourable reaction path has an activation energy of 1.11 eV, only 66% of that on Ni(111). In this dissociation reaction, the CO first tilts towards one of the adjacent Ni terrace atoms, followed by a CO stretch. In this process, the O again moves through the one-fold position on top of that Ni atom. All results of relevance are shown in table 4; ΔE^{tot} refers to energy changes with respect to the equilibrium configuration. On a Ni(110) surface the same reaction mechanism has been calculated through resulting in an activation energy of 0.88 eV; even lower than for the stepped Ni(111) surface. Major part of the differences in activation energy for CO dissociation is not caused by activation of the dissociation reaction, but by changes in the repulsive part of the interactions.

Table 4
Dissociation of relaxed fcc site chemisorbed CO on stepped Ni(111)

ΔE^{tot} (eV)	D (Å)	Z (Å)	L (Å)	
0.00	1.20	2.50	0.00	
0.07	1.19	2.40	0.25	
0.47	1.23	1.70	0.50	
0.88	1.42	1.70	0.77	
1.04	1.52	1.70	1.03	
1.11	1.63	1.70	1.33	
1.00	1.79	1.40	1.57	
0.75	1.89	1.40	1.77	O atop
0.17	2.15	1.40	1.95	
0.02	2.35	1.40	2.16	
0.00	2.54	1.30	2.37	

The increased reactivity of steps and surface defects for CO dissociation on Ni has been reported by Ibach et al. [22], Erley et al. [43], Joyner and Roberts [47], Eastman et al. [48], Erley and Wagner [49], and also for Pt by Li and Vanselow [50].

In conclusion, we have found three new configurations for CO chemisorbed in the vicinity of a step. Of these, the adsorption energy of the relaxed fcc site chemisorbed CO is almost equal to that on the Ni(111) terrace. The complex with the C atom in the fcc step allows the CO to dissociate with an activation energy which is 34% lower than for the complex on Ni(111).

3. Conclusions

Using the ASED-MO method, the adsorption of C, O, and CO on Ni(111) has been described.

For the Ni(111) surface, the exothermic dissociation reaction has an activation energy almost equal to the heat of adsorption. In this reaction, the O atom passes through its most stable adsorption site.

The presence of a monoatomic step with (110) geometry creates three new stable chemisorption complexes. Of these, one allows the CO to dissociate with an activation energy significantly lower than on Ni(111). Major part of the decreased activation energy is caused by weaker repulsive interactions between C and O. The results presented are in excellent agreement with data from the literature.

Acknowledgements

The authors are grateful to Professor Dr. V. Ponec and Dr. A.P.J. Jansen for stimulating discussions. Also, the authors want to acknowledge Professor Dr. A.B. Anderson for supplying a copy of the ASED MO program.

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