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## THEORETICAL STUDIES ON THE INTERACTION OF CO AND HYDROGEN ON Ni (100) SURFACE

By

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### Abstract

Extended Hückel Molecular Orbital (EHMO) calculations have been performed on 5-atom nickel cluster, with CO and hydrogen adsorbed on it in various configurations to arrive at a model for the methanation of CO on Ni(100) surface. The most probable surface species formed due to interaction of CO and hydrogen on Ni(100) surface is speculated, based on the calculated parameters namely, adsorption energy, electronic energy level separation, electron population and the degree of bonding for various configurations. The relevance of these surface species in methanation reaction is also discussed.

### Introduction

Simultaneous activation of CO and hydrogen on transition metals has been extensively investigated<sup>1-4)</sup> to probe the fundamental steps involved in the catalytic hydrocarbon synthesis reactions. Group VIII metals, particularly Fe, Co and Ni have been found to be active catalysts for the reduction of CO and CO<sub>2</sub> by either hydrogen or H<sub>2</sub>O<sup>5-9)</sup>. However, the reduction of CO by hydrogen has been found to be the more viable process for the production of fuel gases like methane. Variety of products have been identified in these reactions. Generally simple hydrocarbons are formed over cobalt surfaces and oxygen containing hydrocarbons are formed on iron surfaces. This behaviour has been attributed to the facile CO insertion to M-H and M-R bonds at the surfaces leading to the chain growth of the hydrocarbons. In contrast, the nickel catalyst has been shown to give selectively methane as the product. Therefore, the mode of adsorption of CO and hydrogen on nickel surface and the surface complex formed thereby must be playing a vital role in this reaction mechanism. Nickel was reported as a methanation

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catalyst<sup>10</sup>) as early as 1902 itself and thereafter numerous studies have been reported<sup>11-16</sup>. Even then there seems to be contradictory views on the possible surface species formed as a result of interaction of CO and hydrogen on nickel surface. Some authors<sup>11-13,58</sup> suggest that the interaction between adsorbed CO and adsorbed hydrogen leads to the formation of surface complex which later gets converted to the products, while others<sup>14-16</sup> suggest that adsorbed CO undergoes dissociation to produce surface carbide which gets reduced by adsorbed hydrogen to form the product. In this communication, the results of the semi-empirical cluster calculations carried out on various possible surface species that may be formed due to step-wise and simultaneous coadsorption of CO and hydrogen have been analysed, with a view to identify the possible intermediate for methanation reaction.

### Method of Calculation

To obtain conclusive and unambiguous information, calculations have to be performed on various possible surface complexes and on all possible modes of adsorption. In order to handle such a large number of configurations, it becomes necessary to restrict our options to semi-empirical calculations. Extended Hückel Molecular Orbital (EHMO) calculations have been performed with Slater Type Orbitals (STO-single- $\zeta$ -functions) as basis functions. The parameters used in the calculations namely orbital exponents and VOIEs are collected from literature<sup>17,18</sup>, and the values of bond distances are taken from Ref. 19. Electron population analysis is performed according to the procedure developed by Mulliken<sup>20</sup>. Armstrong *et al*<sup>21</sup> have developed a method for bonding analysis where in all electrons in a molecule are divided into electrons on atoms  $B_{AA}$  and electrons in bonds  $B_{AB}$ , which are expressed by the following expressions :

$$B_{AA} = 1/2 \sum_{\substack{\lambda \text{ on A} \\ \sigma \text{ on A}}} P_{\lambda\sigma}^2$$

$$B_{AB} = \sum_{\substack{\lambda \text{ on A} \\ \sigma \text{ on B}}} P_{\lambda\sigma}^2$$

where  $P_{\lambda\sigma}$  is the mobile bond order.  $B_{AB}$  is a measure of covalency and it is considered as the 'degree of bonding' between the atoms A and B. Adsorption energy for each mode of adsorption is calculated as the difference between the total one-electron energy of the system and the sum of the atomic energies of all individual atoms.

The difference between the binding energy values of  $4\sigma$  and  $1\pi$  levels of CO adsorbed on Ni(100) has been estimated to be 3.00 eV and that for



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coadsorption of CO and hydrogen to be 3.2 eV by UPS measurements.<sup>59)</sup> However, the value of the difference for  $|4\sigma-1\pi|$  as calculated by EHMO method for the adsorption of CO on Ni(100) has been found to be only 2.196 eV. In order to identify the possible surface complex formed by an estimation of the difference between  $4\sigma$  and  $1\pi$  levels of CO adsorbed with hydrogen (either step-wise or coadsorbed), the calculated values have to be normalized as follows:

$$\text{Normalized } |4\sigma-1\pi| \text{ value} = \frac{\text{Calculated value of } |4\sigma-1\pi|}{2.196} \times 3.00 \text{ eV.}$$

### Cluster Models

Electronic structure of small nickel clusters  $\text{Ni}_x$  (where  $x=2, 3, 4, 5$  and 6) have been calculated by Inglesfield<sup>22)</sup> and Basch *et al.*<sup>29)</sup>. Theoretical studies<sup>24-32)</sup> on adsorption of CO on single nickel atom and on small nickel clusters like  $\text{Ni}_2$  and  $\text{Ni}_3$  have already been reported. Based on the results of these calculations, square planar  $\text{Ni}_4$  cluster with  $D_{4h}$  symmetry is chosen as model in the present calculations to represent the Ni(100) plane. Extensive experimental studies on adsorption of CO on nickel surface have been reported using almost all modern surface analytical techniques such as LEED<sup>33</sup> ~<sup>35,39-41,43,45)</sup>, AES<sup>33,34,37)</sup>, XPS<sup>36,42)</sup>, UPS<sup>36)</sup>, EELS<sup>35,39)</sup>, HREELS<sup>38,43)</sup>, SIMS<sup>44)</sup>, mass spectral<sup>34)</sup>, work function measurements<sup>33,34)</sup>, TPD<sup>45)</sup> and it has been shown

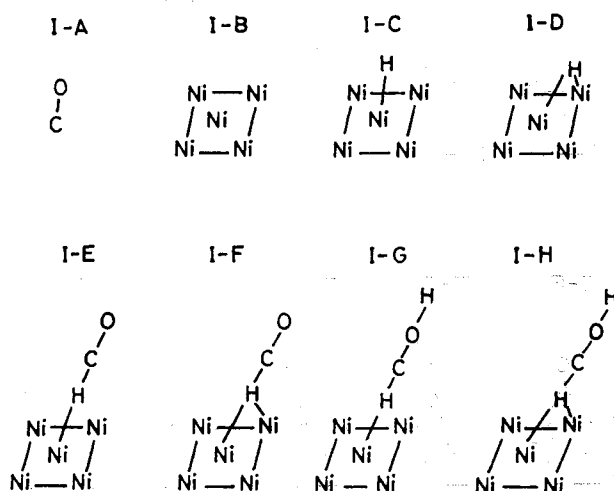


Fig. 1. Structures of clusters considered in Table 1.



that CO adsorbs on Ni(100) in linear mode on a on-top site and in bridged mode on two nearest neighbours. Therefore calculations have been performed on Ni<sub>5</sub> cluster with linearly adsorbed CO (II-A) and Ni<sub>5</sub> cluster with CO adsorbed on bridged site (III-A). The adsorption of hydrogen on nickel has also been studied elaborately both theoretically<sup>46-51</sup> and experimentally<sup>52-55</sup> and it has been shown that the adsorption takes place in atomic form. So

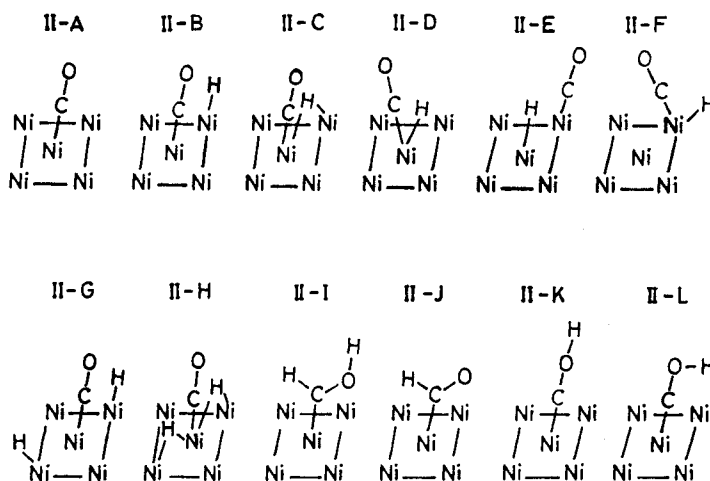


Fig. 2. Structures of clusters considered in Table 2.

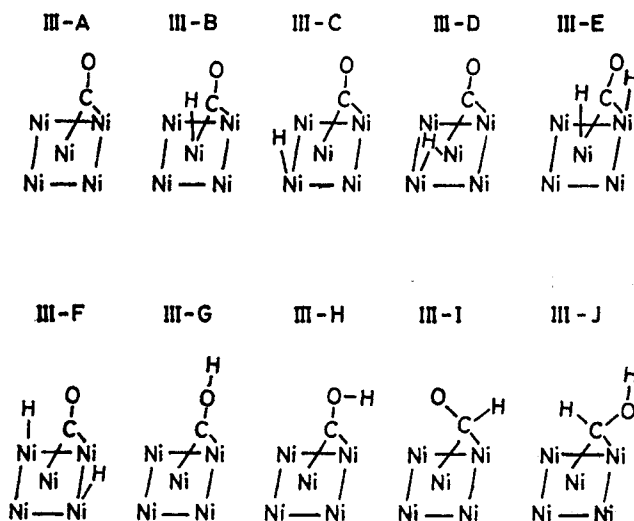


Fig. 3. Structures of clusters considered in Table 3.



TABLE 1. Values of calculated parameters for adsorption of hydrogen on Ni<sub>5</sub> and CO on H presorbed Ni<sub>5</sub>

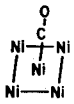
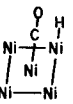
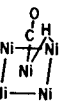
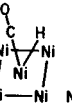
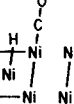
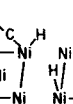
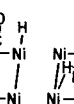
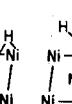
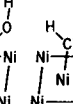
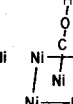
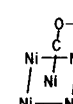
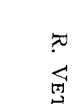
Structure	I-A	I-B	I-C	I-D	I-E	I-F	I-G	I-H
Properties								
Adsorption* energy (eV)	11.484	9.173	4.061	4.982	5.471	6.464	4.713	5.651
Electronic energy levels (eV)								
4σ	-20.468				-21.066	-21.175	-22.396	-22.512
1π	-18.367				-18.340	-18.346	-18.340	-18.346
1π	-18.367				-18.339	-18.342	-18.339	-18.342
5σ	-14.453				-17.139	-17.200	-18.128	-18.194
2π	-9.158				-9.446	-9.566	-9.446	-9.566
2π	-9.158				-9.953	-9.365	-9.446	-9.373
4σ-1π  separation (eV) calculated	2.101				2.726	2.829	4.056	4.166
4σ-1π  Normalized separation (eV) (UPS data)	2.865				3.717	3.858	5.531	5.681
Electron population								
on H			1.587	1.584	0.868	0.901	0.882	0.934
on C	2.998				5.592	5.408	5.557	5.392
on O	7.002				7.388	7.380	6.960	6.949
on CO	10.000				12.980	12.787	12.517	12.340
Degree of bonding between the atoms								
C-O	1.832				0.945	0.951	0.931	0.939
C-H					0.702	0.536	0.807	0.683
O-H					0.014	0.012	0.800	0.799
Ni-C					0.331	0.545	0.279	0.455
Ni-H			0.569	0.533	0.140	0.137	0.094	0.097
Ni-O					0.032	0.038	0.029	0.030

\* The values for structures I-A and I-B are simply the atomization energies.

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TABLE 2. Values of calculated parameters for coadsorption of hydrogen and linear carbon monoxide

Structure	II-A	II-B	II-C	II-D	II-E	II-F	II-G	II-H	II-I	II-J	II-K	II-L
Properties												
Adsorption energy (eV)	6.589	12.374	9.034	9.355	11.155	12.394	17.850	11.421	6.978	11.939	4.701	3.794
Electronic energy levels (eV)												
4σ	-20.541	-20.562	-21.155	-21.049	-20.966	-20.561	-20.585	-21.285	-21.893	-20.556	-22.098	-21.414
1π	-18.345	-18.348	-18.377	-18.379	-18.346	-18.370	-18.378	-18.407	-19.053	-18.472	-18.345	-18.922
1π	-18.345	-18.331	-18.345	-18.346	-18.329	-18.333	-18.345	-18.345	-18.344	-18.344	-18.345	-18.345
5σ	-15.283	-15.488	-16.996	-16.882	-16.655	-15.717	-15.787	-17.290	-17.037	-15.676	-15.401	-15.340
2π	-9.709	-9.749	-9.708	-9.718	-9.515	-10.037	-9.709	-10.103	-9.657	-9.657	-9.709	-9.717
2π	-9.709	-9.573	-9.418	-9.471	-9.455	-9.618	-8.956	-9.709	-9.266	-9.575	-9.708	-9.709
4σ-1π  separation calculated (eV)	2.196	2.214	2.778	2.670	2.620	2.191	2.207	2.878	2.840	2.084	3.753	2.492
4σ-1π  normalized separation (eV) (UPS data)	3.000	3.019	3.788	3.641	3.573	2.988	3.010	3.925	3.873	2.842	5.118	3.398
Electron population												
on H		1.655	1.200	1.220	1.591	1.668	1.639	1.254	0.978	1.408	0.491	0.542
on C	5.609	5.841	4.977	4.920	5.984	5.740	5.894	4.787	5.107	4.843	5.639	5.493
on O	7.410	7.437	7.371	7.385	7.492	7.459	7.439	7.347	7.009	7.388	6.893	7.050
on CO	13.019	13.278	12.348	12.305	13.476	13.199	13.333	12.134	12.116	12.231	12.532	12.544
Degree of bonding between the atoms												
C-O	0.943	0.923	0.997	0.985	0.845	0.878	0.924	1.028	0.925	0.975	0.967	0.925
C-H		0.004	0.380	0.435	0.138	0.139	0.001	0.232	0.962	0.758	0.026	0.181
O-H		0.001	0.022	0.030	0.027	0.017	0.001	0.013	0.779	0.071	0.811	0.619
Ni-C	1.151	1.039	1.094	0.909	1.016	0.917	1.004	0.998	0.834	0.805	1.142	1.056
Ni-H		0.784	0.302	0.307	0.576	0.681	0.803	0.374	0.009	0.040	0.003	0.039
Ni-O	0.066	0.054	0.075	0.066	0.046	0.064	0.052	0.068	0.031	0.044	0.070	0.085

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TABLE 3. Values of calculated parameters for coadsorption of hydrogen and bridged carbon monoxide

Structure	III-A	III-B	III-C	III-D	III-E	III-F	III-G	III-H	III-I	III-J
Properties										
Adsorption energy (eV)	7.830	9.431	13.709	11.539	10.874	19.714	5.945	6.235	11.068	8.263
Electronic energy levels (eV)										
4σ	-20.570	-20.847	-20.583	-21.121	-21.410	-20.584	-22.106	-21.479	-20.720	-21.972
1π	-18.350	-18.658	-18.351	-18.362	-18.438	-18.369	-18.350	-18.932	-18.477	-19.099
1π	-18.347	-18.347	-18.348	-18.347	-18.342	-18.355	-18.347	-18.348	-18.346	-18.346
5σ	-15.463	-16.054	-15.615	-16.889	-17.312	-15.691	-15.579	-15.528	-16.206	-17.105
2π	-10.114	-9.733	-9.886	-9.733	-9.689	-9.794	-9.733	-9.733	-9.714	-9.715
2π	-9.733	-9.336	-9.733	-9.515	-9.564	-9.304	-9.220	-9.277	-9.535	-9.485
4σ-1π  separation (eV) calculated	2.220	2.189	2.232	2.759	2.972	2.215	3.756	2.547	2.243	2.873
4σ-1π  normalized separation (eV) (UPS data)	3.000	2.985	3.044	3.762	4.053	3.020	5.122	3.473	3.059	3.918
Electron population										
on H		1.091	1.631	1.437	1.158	1.641	0.484	0.552	1.274	1.013
on C	5.626	4.931	5.633	5.569	4.458	5.861	5.650	5.503	4.923	5.048
on O	7.445	7.434	7.446	7.479	7.344	7.466	6.926	7.081	7.396	6.998
on CO	13.070	12.365	12.780	13.048	11.802	13.327	12.576	12.584	12.318	12.046
Degree of bonding between the atoms										
C-O	0.926	0.937	0.924	0.851	1.044	0.909	0.946	0.919	0.966	0.919
C-H		0.678	0.010	0.253	0.494	0.005	0.024	0.196	0.814	0.899
O-H		0.010	0.001	0.020	0.029	0.001	0.813	0.604	0.046	0.781
Ni-C	0.887	0.735	0.882	0.791	0.464	0.869	0.884	0.810	0.788	0.706
Ni-H		0.228	0.781	0.375	0.417	0.798	0.002	0.035	0.102	0.071
Ni-O	0.043	0.048	0.042	0.046	0.037	0.036	0.046	0.072	0.149	0.135

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calculations for the  $\text{Ni}_5\text{H}$  cluster with hydrogen on on-top site (I-C) and on bridge site (I-D) have also been performed. Calculations have also been carried out on  $\text{Ni}_5$  cluster with CO on on-top site or bridge site with one or two hydrogens included at various possible positions, to study the situation of coadsorption/step-wise adsorption of CO and hydrogen on Ni(100). Various surface complexes that have been proposed as intermediates for methanation reaction have been considered. The geometry of the clusters considered are shown in Figs. 1, 2 and 3 and the results obtained are summarized in Tables 1, 2 and 3.

### Results and Discussion

In theoretical calculations for chemisorption, the calculated quantities like electronic energy levels, adsorption energy etc., are always related to values for free molecules which are experimentally known. For free CO, the electronic energy level ordering calculated by this procedure is same as predicted by less approximate calculations<sup>50)</sup> and the calculation predicts ionization energies well. The calculations performed for  $\text{Ni}_5$  cluster have yielded similar atomic populations as for the square pyramidal  $\text{Ni}_5$  cluster reported in the literature.<sup>29)</sup> The results of calculations for the adsorption of hydrogen on both on-top and bridge sites are in accordance with the previous reports<sup>49)</sup> <sup>50)</sup>. Calculations for configurations representing the linear and bridged mode of adsorption of CO (II-A and III-A respectively) show that the ordering of CO energy levels do not alter due to adsorption, though the stabilization of energy levels of CO is significant due to interaction with nickel 'd' orbitals. There is significant amount of electron transfer from metal 'd' levels to CO which probably facilitates the dissociation of CO. These results are also in agreement with previous theoretical calculations<sup>25,32,57)</sup>.

#### 1) *Adsorption of CO on hydrogen presorbed surface*

Calculations have been carried out for configurations representing the adsorption of CO on hydrogen presorbed Ni(100) surface. The configurations are shown in Fig. 1 and their significant energy levels and the values of calculated parameters are given in Table 1. The adsorption energies for these configurations are invariably small compared to adsorption energies for configurations (Fig. 2 and 3) representing hydrogen adsorption on CO presorbed Ni(100) given in Tables 2 and 3. Electron population analysis shows that there is transfer of metal electrons to the adsorbates though not to any significant amount. In presence of adsorbed hydrogen the transfer of metal electrons to CO is small. The bonding analysis reveals that in these com-



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plexes, the main interaction is between metal and carbon only, though they are not directly bonded. However, Ni-C interaction is considerably less than the cases where carbon is directly linked to metal. Though the hydrogen is directly linked to metal  $B_{\text{Ni-H}}$  values (Table 1) are low and hence these complexes are not stabilized. In addition, the difference between the energy levels  $4\sigma$  and  $1\pi$  for these configurations are not in correspondence with the observed UPS spectral data<sup>59</sup> (3.2 eV) for CO and hydrogen coadsorbed on Ni(100) surface. This points out that these may not be the structures of surface species formed.

2) *Adsorption of hydrogen on CO covered surface*

The configurations considered are shown in Figs. 2 and 3 and the results obtained for them from the EHMO calculations are given in Tables 2 and 3. Generally these configurations are found to have larger adsorption energy than the configurations considered in Table 1.

2. a) *Coadsorption of hydrogen and linear CO*

Various structures considered are given in Fig. 2 and their calculated parameters are given in Table 2. Among them six surface species appear to be more probable, since their adsorption energies are higher than those of other configurations. These entities include structures II-G and II-H, where two hydrogen atoms are adsorbed adjacent to CO, II-J which is a surface aldehydic complex and II-B, II-E and II-F where CO and hydrogen are adsorbed at same or different sites. UPS spectral data for the adsorption of CO and for coadsorption of CO and hydrogen on Ni(100) have been reported by Koel *et al.*<sup>60</sup>. The  $|4\sigma-1\pi|$  separation reported by them for adsorption of CO is 3.0 eV and for coadsorption of CO and hydrogen is 3.2 eV. Calculated  $|4\sigma-1\pi|$  separation for  $\text{Ni}_5\text{CO}$  is found to be 2.196 eV instead of the experimental value of 3.0 eV. On this basis, the calculated values of  $|4\sigma-1\pi|$  separation for all the configurations have been normalized and compared with the reported value of 3.2 eV. Though II-E, II-F, II-H and II-J have favourable adsorption energy,  $|4\sigma-1\pi|$  separation is not in accordance with experimental value. The  $|4\sigma-1\pi|$  separation for II-B, II-G and II-L are found to be almost as expected. The species with the structure II-L is not probable since the adsorption energy is low. Electron population analysis for these configurations shows that there is always flow of electrons from metal to CO and hydrogen and hence carbon and oxygen are negatively charged and thus favours easy dissociation of C-O bond. Electron populations on adsorbates are extremely high for the configurations II-B, II-E and II-G. Results of bonding analysis, namely the degree of bonding (B) between



any two atoms in the considered species are also given in Table 2.  $B_{C-O}$  has decreased for all the structures of the surface species compared to the values in gaseous CO (1.8313) and  $B_{Ni-C}$  is around 1 for almost all cases.  $B_{Ni-O}$  is not significant however. Strong bonding of hydrogen either to carbon or oxygen decreases the flow of electron from metal to CO. So the configurations with minimum  $B_{C-H}$  and  $B_{O-H}$  values are expected to undergo easy dissociation and thereby undergo easy methanation. On this basis also II-B and II-G can be considered to be the favourable structures. Therefore it is reasonable to propose that one or two hydrogen atoms adsorbing on nickel atoms adjacent to linearly adsorbed CO on a  $Ni_3$  cluster (II-B and II-G) are the favourable modes of adsorption. Structure II-G is more probable than II-B, since the adsorption energy predicted for II-G is much higher.

## 2. b) Coadsorption of hydrogen and bridged CO

Various configurations representing the coadsorption of hydrogen with CO on bridge site are shown in Fig. 3 and the results of the calculations on them are given in Table 3. The adsorption energies are significantly high for the configurations III-C, III-D, III-E, III-F and III-I. On the basis of  $|4\sigma-1\pi|$  separations, the configurations III-C, III-F, III-H and III-I can be considered to be the probable surface species. Electron population analysis reveals that there is maximum transfer of electrons from metal to adsorbates only in the case of III-F. Bonding analysis shows that the degree of bonding between nickel and carbon  $B_{Ni-C}$  is almost the same and  $B_{C-O}$  is around 1 for all the structures. The bonding of carbon and oxygen to hydrogen ( $B_{C-H}$  and  $B_{O-H}$ ) are minimum for the structure III-F indicating the least hindrance for the flow of electrons from metal to CO. So it is considered that III-F is the favourable mode of adsorption of hydrogen to the Ni(100) with presorbed CO in the bridged site.

## Conclusions

Based on these results, it may be concluded that the probable surface species formed during the interaction of CO and hydrogen on nickel surface are II-G and III-F and they are shown in Fig. 4. They have favourable adsorption energy and the  $|4\sigma-1\pi|$  separation values are in accordance with UPS measurements.<sup>59</sup> Electron densities for these configurations show that both carbon and oxygen are negatively charged leading to easy dissociation. Probably these initial surface species may give rise to  $-CH_2$  species. This  $-CH_2$  species later interacts with gas phase hydrogen and desorbs as  $CH_4$  as shown in Fig. 5. Calculations have also been performed for the structures









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TABLE 4. Values of calculated parameters for the intermediates ( $-\text{CH}_2$ ) adsorbed on Ni(100)

Properties	Structure	IV-A	IV-B
			
Adsorption energy (eV)		16.320	17.132
Electron population	on C	5.942	5.942
	on H	0.926	0.961
Degree of bonding between atoms	M-C	0.694	0.551
	C-H	0.963	0.904
	M-H	0.013	0.008

combines with  $-\text{CH}_2$  species to produce  $\text{CH}_4$  can be a vital step in the reaction sequence. However, EHMO calculations can not give information on the values of the activation energy for various steps involved in the process.

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