INTERACTION OF CARBON MONOXIDE AND HYDROGEN WITH α-IRON(100) SURFACE

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Summary

The interactions of carbon monoxide and hydrogen during their individual and mixed adsorption on Fe(100) surface has been studied through Extended Hückel Molecular Orbital (EHMO) calculations. Based on the results, a two-carbon complex representing the adsorption of carbon monoxide over partially hydrogenated carbon is proposed as the catalytic precursor in the chain-growth process of the Fischer–Tropsch (FT) synthesis.

Introduction

Iron in various forms [1 - 6] has been extensively used as a catalyst for the synthesis of hydrocarbons from oxides of carbon by the Fischer–Tropsch (FT) process, since it is thus possible to obtain a desired product distribution by varying reaction conditions [7 - 9] such as temperature, ratio of gaseous reactants and space velocity. In spite of the wide use of iron catalysts for FT synthesis, details on the nature of the precursors for the product formation are still not clear. Various types of surface intermediates, including the formation of iron carbide, have been proposed [10, 11] and their role in the catalytic synthesis of higher hydrocarbons ($>C_4$) has also been considered. Modelling studies [5, 12] with iron carbonyl and carbonyl-carbide clusters have indicated that the clusters are involved in the stoichiometric reduction of CO and in the coupling of CO with carbidic carbon to produce C_2 moieties. The present communication deals with the results obtained by model calculations carried out on the adsorption and coadsorption of carbon monoxide and hydrogen on iron clusters representing the Fe(100) surface, with a view to obtaining further information on the nature of the surface intermediates formed during hydrocarbon synthesis.

Cluster models and calculation procedures

Though iron exists in both fcc and bcc lattices, under the conditions of hydrocarbon synthesis it always exists in the bcc lattice (α-form) [7].

Further, the stabilization energy of the five-atom cluster with D_{4h} symmetry having all the atoms in the same plane which represents fcc-Fe(100) [-12.178 eV] is less than that of the five-atom cluster with C_{4v} symmetry which represents bcc-Fe(100) [-13.887 eV]. The binding energies for the adsorption of carbon monoxide and hydrogen on the fcc-Fe(100) cluster are also less than those on bcc-Fe(100). Therefore a five-atom $Fe_5(4,1)$ cluster, having four atoms in a plane and a single atom below the plane with C_{4v} symmetry, has been considered for the calculations. Different adsorption sites, namely above the centre atom, bridging, and on the corner atom, are taken into consideration. Chemisorption of carbon monoxide and hydrogen on iron catalysts has been reported [2] to cause only localized changes on the surface; thus it is reasonable to choose a cluster containing as few as five atoms to study the effects of chemisorption. The metal–carbon distance (1.81 Å) is considered as the distance between the surface plane and carbon, to maintain uniformity among the three sites considered.

The Extended Hückel Molecular Orbital (EHMO) method has been used for the calculations, since the number of configurations considered is large. The details of the calculation procedure are given elsewhere [13]. Adsorption energy is calculated as the difference between the total energy of the system and the sum of the atomic energies of all individual atoms. The calculated parameters, such as adsorption energy and formal charges, are emphasized slightly more than the absolute values since the effects of core electrons and electron–electron repulsions are neglected in the approximation. In spite of the approximations involved in the method, it is well-parameterised, so that reliable SCF wave functions are obtained and the various calculated parameters, such as MO energy levels, charges on atoms and atomic overlap population, have been shown [14, 15] to be fairly quantitative. Successful studies [16, 17] which treat chemisorption and adsorption of complexes by this method provide the necessary encouragement for applying this procedure to adsorption phenomena. Recently, Ruckenstein and Halachev [18] have explained the observed LEED patterns of CO adsorbed on Rh(111) based on the results of their EHMO calculations. The trend of adsorption energies is predicted correctly and the stable modes of adsorption can therefore be deduced from these calculations. The required parameters, such as valence orbital ionisation energies (VOIEs) and orbital exponents, were collected from refs. 19 and 20 respectively.

Results and discussion

Individual adsorption of carbon monoxide and hydrogen

Carbon monoxide adsorbs associatively on iron surfaces at low temperatures, though considerable dissociation has been observed at higher temperatures [21] or in the presence of surface defects [22]. The adsorption of hydrogen on iron single-crystal surfaces has been found to be dissociative
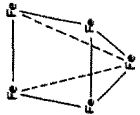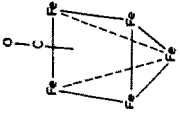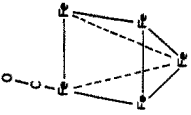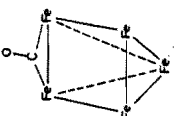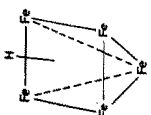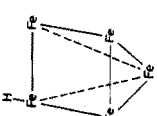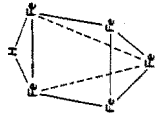
[23 - 25]. The calculated values of parameters such as adsorption energy, the position of individual molecular levels, the degree of bonding between atoms and the formal charges on various atoms are given in Table 1 for CO, the Fe_5-cluster and various configurations representing the individual adsorption of carbon monoxide and hydrogen on various sites of the bcc surface of a five-atom iron cluster. The presence of a negative charge on the adsorbed CO and hydrogen accounts for the experimental observation [25] of an increase in the work function due to adsorption of these gases. The adsorption of hydrogen on bridge and corner sites seems to be more favourable than on the centre site. In the case of carbon monoxide, the order of the molecular levels is unperturbed due to adsorption. However, the 2s orbital of iron lies between the 5σ and 2π levels of carbon monoxide. The degeneracy of 1π levels of carbon monoxide remains unaffected, while 2π levels lose their degeneracy due to adsorption over iron. According to the calculations, the 1π, 5σ and 2π levels are well separated which is in agreement with the reported [26] UPS data on the α-Fe(100) surface. The order of preference among the three sites, based on binding energies, is bridged > corner > centre. However, the values of the binding energies are almost the same for all the three configurations, and it is therefore probable that CO adsorbs in more than one configuration on this surface. The calculated binding energies of CO on iron are larger than those on cobalt and nickel [27, 13], which is in accordance with the experimental observation [28] that carbide formation occurs more readily on an iron surface compared to cobalt and nickel surfaces.

Simultaneous adsorption of carbon monoxide and hydrogen
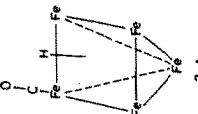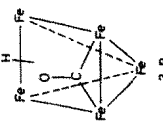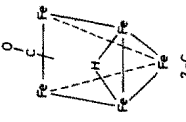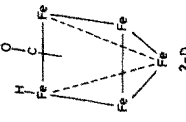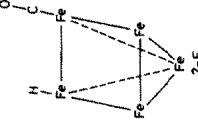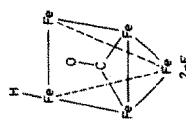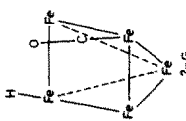   *Adsorption of CO and H on different sites*
    Calculations have been performed for configurations representing the adsorption of carbon monoxide and hydrogen on any two different sites. Seven possible configurations were considered; the different configurations considered and the values of the parameters calculated are given in Table 2. The adsorption energies for the configurations 2-A, 2-B, 2-C and 2-D are nearer to the value of the adsorption energy of CO alone on any of the three sites. In other cases where hydrogen is at the corner site, the adsorption energies are higher than the value of the adsorption energy of CO alone. The degeneracy of the 1π levels is affected slightly, while that of the 2π levels is completely lost. The 1s orbital of hydrogen and the 4s orbital of iron interact with the 2π levels and stabilise them. The adsorption energy is found to be high for the configurations in which there is maximum electronic charge transfer from metal to adsorbates. Bonding analysis reveals that the degree of bonding of metal with carbon monoxide and hydrogen adsorbed simultaneously is almost the same as in the case of their individual adsorptions. There is also not much bonding interaction between the adsorbates in any of these configurations. Hence these configurations for the simultaneous adsorption of carbon monoxide and hydrogen at different sites may not have much relevance in the synthesis of hydrocarbons.

TABLE 1

Values of calculated parameters for CO, Fe_5-cluster, CO adsorbed on three sites of an Fe_5-cluster and H adsorbed on three sites of an Fe_5-cluster

Properties	Structures							
	1-A	1-B	1-C	1-D	1-E	1-F	1-G	1-H
Adsorption* energy (eV)	11.484	13.887	30.045	31.106	31.853	16.470	19.500	18.733
Electronic energy levels (eV)								
4σ	−20.468		−20.544	−20.564	−20.585			
1π	−18.367		−18.299	−18.298	−18.303			
1π	−18.367		−18.299	−18.298	−18.301			
5σ	−14.453		−15.330	−15.499	−15.706			
4s(Fe)			−10.352	−11.123	−10.763			
2π	−9.158		−10.084	−9.867	−10.260			
2π	−9.158		−10.084	−9.716	−9.674			
Degree of bonding between the atoms								
M—H						0.187	0.799	0.407
M—C			0.457	1.492	0.999			
M—O			0.030	0.001	0.054			
C—O	1.832		0.928	0.912	0.911			
Formal charges on various atoms								
C	+1.002		−1.509	−1.700	−1.426			
O	−1.002		−1.410	−1.450	−1.457			
H						−0.656	−0.583	−0.447

*Values for structures A and B are simply the atomization energies.

249

TABLE 2

Values of calculated parameters for configurations representing coadsorption of CO and H at different sites of an Fe$_5$-cluster

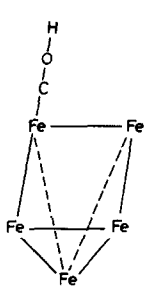| Properties	Structures						
	2-A	2-B	2-C	2-D	2-E	2-F	2-G
Adsorption energy (eV)	33.386	32.827	33.130	33.900	36.337	37.311	36.755
Electronic energy levels (eV)							
4σ	−21.058	−20.789	−21.164	−20.573	−20.595	−20.624	−20.611
1π	−18.341	−18.653	−18.347	−18.347	−18.304	−18.306	−18.298
1π	−18.298	−18.303	−18.299	−18.298	−18.298	−18.302	−18.298
5σ	−16.799	−16.134	−17.083	−15.757	−15.579	−15.974	−15.828
1s(H)	−12.081	−12.109	−11.453	−13.671	−14.227	−14.094	−14.128
4s(Fe)	−10.395	−10.260	−10.313	−10.332	−10.719	−10.402	−10.608
2π	−9.867	−10.188	−10.084	−10.084	−9.742	−10.129	−9.867
2π	−8.825	−8.741	−8.993	−8.993	−9.653	−9.654	−9.706
Degree of bonding between the atoms							
M—C	1.403	0.787	0.524	0.694	1.499	1.015	1.480
M—O	0.087	0.040	0.040	0.060	0.086	0.057	0.089
M—H	0.150	0.088	0.040	0.815	0.791	0.791	0.773
C—O	0.927	0.910	0.910	0.949	0.891	0.903	0.903
C—H	0.435	0.685	0.220	0.040	0.015	0.015	0.025
O—H	0.035	0.004	0.024	0.002	0.008	0.002	0.003
Formal charges on various atoms							
C	−0.972	−0.740	−1.207	−1.332	−1.781	−1.460	−1.695
O	−1.429	−1.461	−1.411	−1.391	−1.450	−1.461	−1.454
H	−0.310	−0.064	−0.232	−0.551	−0.572	−0.590	−0.580

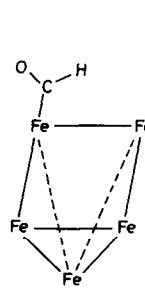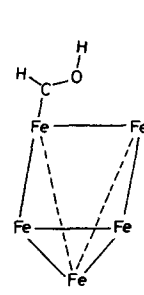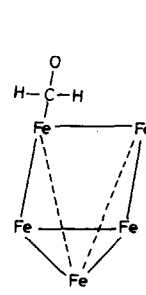*Surface complexes due to coadsorption of CO and H*
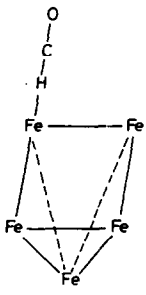
Calculations have also been performed on various possible surface complexes that may be formed due to coadsorption of carbon monoxide and hydrogen on $Fe_5(4,1)$ clusters. Adsorption of these complexes on three different sites, namely corner, centre and bridging, is considered, and the various configurations with the results obtained from parameter calculations are given in Tables 3 - 5 for the three sites respectively. The order of preference for adsorption of these complexes at various sites is bridged > corner > centre. Among all these configurations, the complex formed due to the adsorption of carbon monoxide above hydrogen presorbed on the surface (structure A) has the lowest adsorption energy, indicating that such a surface species is improbable. The alcoholic types of complexes (structures B and D) also do not have a favourable adsorption energy. Aldehydic and ketonic type complexes (structures C and E) have a higher adsorption energy at the corner site. The degeneracy of the 1π levels is lost in these complexes if the M—C—O bond angle is varied from 180°, otherwise the degeneracy is almost maintained. There is a strong interaction of the 5σ and 2π orbitals of carbon monoxide with the 1s orbital of hydrogen and the 4s orbital of iron. The hydrogen atom has a positive charge when it is not bonded to the metal atom. The formal charges on carbon and oxygen are always negative. The degree of bonding and the overlap population values show that the bonding between metal and oxygen is weak or even repulsive. However, the repulsion is smaller in the case of iron in comparison to cobalt and nickel. Therefore, oxygen-containing complexes are more stable over iron catalysts than over other metal catalysts, and this could be the reason for the selective formation of oxygenated hydrocarbons on iron catalysts. The present results indicate that structures 3-C, 3-E, 4-E and 5-E are the most probable surface complexes; these conclusions are also supported by IR reports [29] which show bands due to the stretching frequencies of C—H and C—O bonds.

Two-carbon complex as a possible intermediate

It is also possible that a two-carbon complex is formed by adsorption of CO on top of the partially-hydrogenated carbon layer. The particular two-carbon complex shown in Table 6 has been chosen because Blyholder and Emmett [30] have proposed that this type of ketene complex can be a nucleus for chain growth, based on studies of the incorporation of radio-active alcohols [31] and aldehydes [32] in the reaction mixture. The values of the various parameters calculated for the ketene-type complex on three different sites are given in Table 6. These have a favourable binding energy, which is higher than any of the other configurations considered in Tables 3 - 5. Since in this complex, the distance between oxygen and metal is greater, the Fe—O repulsive interaction is at a minimum. There are strong interactions among the metal and adsorbate atoms, as indicated by the thorough mixing and reordering of the energy levels. The 1π orbitals of CO become destabilised and the 2π orbitals merge with the 'd' band of the metal. The formal atomic charges of these complexes show that the
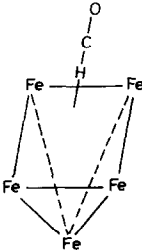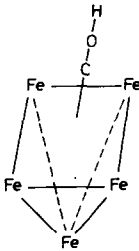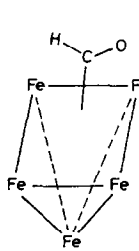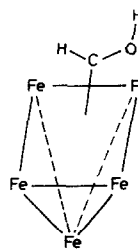
TABLE 3

Values of calculated parameters for configurations in which various complexes considered are adsorbed at the corner site of an Fe_5-cluster

Properties	Structures				
	3-A	3-B	3-C	3-D	3-E
Adsorption energy (eV)	30.929	30.048	35.689	32.547	35.189
Electronic energy levels (eV)					
4σ	−20.590	−22.115	−20.538	−21.876	−21.511
1π	−18.295	−18.298	−18.461	−19.044	−18.884
1π	−18.295	−18.298	−18.338	−18.338	−18.298
5σ	−16.428	−15.605	−15.691	−17.043	−16.857
1s(H)	−11.440	−11.123	−14.031	−11.784	−13.761
4s(Fe)	−10.299	−9.867	−11.110	−10.912	−11.096
2π	−9.614	−9.715	−9.539	−9.592	−9.788
2π	−9.554	−8.737	−8.739	−8.738	−8.743
Degree of bonding between the atoms					
M—C	0.405	1.486	1.064	1.093	0.712
M—O	0.043	0.088	0.079	0.061	0.067
M—H	0.565	0.004	0.031	0.025	0.117
C—O	0.727	0.936	0.982	0.922	0.877
C—H	0.152	0.025	0.777	0.947	0.813
O—H	0.097	0.811	0.070	0.779	0.005
Formal charges on various atoms					
C	−2.414	−1.728	−0.759	−1.034	−0.545
O	−1.525	−0.931	−1.396	−1.021	−1.490
H	−0.612	+0.520	−0.412	+0.578	+0.106

hydrogen atoms are positively charged since they are not bonded to metal atoms. The carbon atom between the —CH_2 group and the oxygen atom is also positively charged, in contrast to the negative charge on the carbon in the adsorption of pure CO. However, if one considers the complex as CO adsorbed on a carbon layer, the overall charge on CO is negative, due to the greater negative charge on the oxygen atom. The degree of bonding of metal
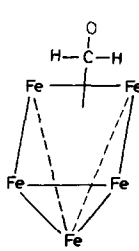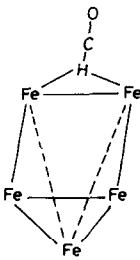
TABLE 4

Values of calculated parameters for configurations in which various complexes considered are adsorbed at the centre site of an Fe_5-cluster

Properties	Structures				
	4-A	4-B	4-C	4-D	4-E
Adsorption energy (eV)	29.731	28.922	25.102	30.728	34.263
Electronic energy levels (eV)					
4σ	−21.051	−22.081	−20.537	−21.843	−21.425
1π	−18.296	−18.299	−18.465	−19.048	−18.892
1π	−18.296	−18.299	−18.343	−18.343	−18.299
5σ	−17.178	−15.445	−14.722	−17.038	−16.849
1s(H)	−11.014	−10.352	−13.705	−11.876	−13.854
2π	−9.749	−10.088	−10.501	−9.930	−10.551
2π	−9.749	−10.088	−9.825	−9.826	−10.084
4s(Fe)	−8.730	−8.726	−8.731	−8.731	−8.727
Degree of bonding between the atoms					
M—C	0.210	0.457	0.347	0.315	0.238
M—O	0.021	0.030	0.040	0.028	0.028
M—H	0.027	0.001	0.032	0.002	0.058
C—O	0.941	0.952	0.998	0.930	0.888
C—H	0.793	0.026	0.760	0.952	0.809
O—H	0.015	0.809	0.077	0.778	0.005
Formal charges on various atoms					
C	+1.423	−1.543	−0.733	−1.043	−0.343
O	−1.388	−0.900	−1.353	−0.989	−1.462
H	+0.180	+0.527	−0.382	+0.576	+0.135

with either oxygen or hydrogen is small, since they are not directly bonded. Compared to the other configurations shown in Tables 2 - 5, these configurations have a weak M—C bond and a strong C—C bond. These results clearly demonstrate the facile chain growth through this type of complex and the easy desorption of the products.
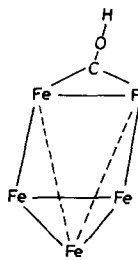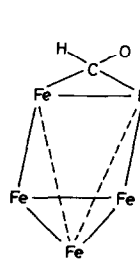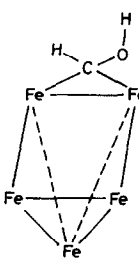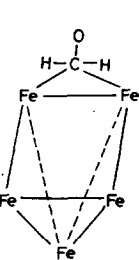
TABLE 5

Values of calculated parameters for configurations in which various complexes considered are adsorbed at a bridge site of an Fe_5-cluster

Properties	Structures				
	5-A	5-B	5-C*	5-D	5-E
Adsorption energy (ev)	31.653	30.772		33.805	36.022
Electronic energy levels (eV)					
4σ	−21.199	−22.082		−22.144	−21.632
1π	−18.303	−18.303		−19.012	−18.914
1π	−18.300	−18.301		−18.343	−18.301
5σ	−17.302	−15.811		−17.122	−16.905
$1s(H)$	−10.800	−10.764		−11.848	−13.906
2π	−10.215	−10.259		−10.557	−10.789
2π	−9.656	−9.674		−9.494	−9.676
$4s(Fe)$	−8.848	−8.740		−8.743	−8.866
Degree of bonding between the atoms					
M—C	0.777	0.100		0.891	0.588
M—O	0.046	0.054		0.245	0.044
M—H	0.160	0.002		0.149	0.227
C—O	0.923	0.931		0.881	0.891
C—H	0.450	0.024		0.809	0.658
O—H	0.010	0.809		0.845	0.005
Formal charges on various atoms					
C	−1.190	−1.447		−0.966	−0.481
O	−1.413	−0.945		−0.959	−1.483
H	+0.112	+0.518		+0.495	+0.053
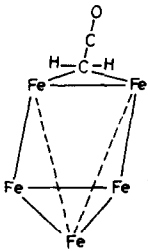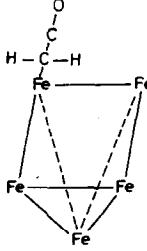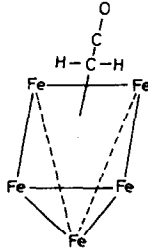
*Calculations for this configuration were not performed due to problems in convergence.

Precursors for the formation of surface intermediates

The probable path of formation of the proposed two-carbon surface complex is analyzed by performing calculations for clusters representing the adsorption of carbon and oxygen, thus representing the carbide and oxide formation respectively. From the results of PES studies, Textor *et al.* [33]

TABLE 6

Values of calculated parameters for configurations in which a two-carbon complex is adsorbed at three possible sites of an Fe_5-cluster

Properties	Structures		
	6-A	6-B	6-C
Adsorption energy (eV)	39.880	39.240	37.639
Electronic energy levels (eV)			
4σ	−26.060	−25.680	−25.446
5σ	−19.199	−19.196	−19.192
1π	−18.347	−18.336	−18.339
1π	−18.300	−18.298	−18.299
1s(H)	−16.077	−15.992	−16.026
$p\sigma$(C)	−14.717	−14.690	−14.681
$p\pi$(C)	−12.607	−12.567	−12.626
4s(Fe)	−10.541	−11.067	−10.456
3d(Fe)	−8.848	−8.750	−8.756
Degree of bonding between the atoms			
M—C	0.342	0.421	0.114
M—O	0.026	0.018	0.009
M—H	0.024	0.085	0.044
C—O	1.256	1.310	1.300
C—H	0.592	0.712	0.722
C—C	1.792	1.828	1.784
Formal charges on various atoms			
H	+0.113	+0.180	+0.199
C*	−0.608	−0.569	−0.538
C	+0.969	+1.207	+1.197
O	−1.239	−1.222	−1.222

C* is the carbon to which two hydrogen atoms are attached.

have reported that dissociative adsorption of CO leads to the formation of carbide and oxide overlayers. It can be seen from the adsorption energies (Table 7) that the formation of carbide, oxide and further hydrogenated carbon species, such as —CH and —CH_2, is energetically favourable. There-fore, dissociated CO which is subsequently hydrogenated can function as

TABLE 7

Adsorption energies (eV) for various possible precursors adsorbed at different sites

Adsorbed species	Adsorption site		
	centre	corner	bridge
carbide	−23.85	−24.88	−24.94
oxide	−31.65	−31.95	−31.53
—CH	−27.82	−28.34	−28.31
—CH$_2$	−28.79	−30.27	−30.11

a precursor for chain growth. Chain growth may occur by the adsorption of molecular CO on these precursors, which subsequently are reduced.

Conclusions

These calculations have indicated that —CH—O, —CH$_2$—O and —CH$_2$—C—O type surface species are the most probable on the basis of the adsorption energy values. These species may take up hydrogen to form alkoxy groups, namely CH$_3$O— and CH$_3$—CH$_2$—O—. These types of alkoxy groups have been reported [34] to exist on Fe(100) surfaces when exposed to CH$_3$OH and C$_2$H$_5$OH. Therefore, it may be concluded that these alkoxy groups are further hydrogenated to give oxygenates over Fe(100) surfaces.

Acknowledgement

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