Journal of
Nanoscience and Nanotechnology
Vol. 10, 5490–5494, 2010

The Structures and Magnetic Moments of Co–C Clusters

Qing-Min Ma, Ying Liu*, Zun Xie, and Jing Wang

Department of Physics, and Hebei Advanced Thin Film Laboratory, Hebei Normal University, Shijiazhuang 050016, Hebei, China; National Key Laboratory for Materials Simulation and Design, Beijing 100084, China

The geometries, binding energies, and magnetic moments of small CoC_N ($N = 1$–8) and Co_2C_N ($N = 1$–6) clusters are studied systematically using all-electron density functional theory (DFT) with the generalized gradient approximation (GGA). The results indicate that, for the CoC_N ($N = 1$–8) and Co_2C_N ($N = 1$–6) clusters, the lowest-energy structures are predicted to be linear structures except for CoC_2 and CoC_7. The ground states of the CoC_N ($N = 1$–8) clusters are linear geometries (C_v) with Co atom at one end. The ground states of the Co_2C_N ($N = 1$–6) clusters are linear geometries (D_h) with the two Co atoms located at the two ends. For all the clusters, analysis of the Mülliken population shows that charge transfers from the Co atom(s) to the C atoms. The magnetic moment lies primarily on the Co atom(s).

Keywords: Density Functional Theory, Cobalt–Carbon Clusters, Geometric Structures.

1. INTRODUCTION

The transition-metal (TM) carbide clusters have been attracting much attention especially after the discovery of the metallocarbohedrenes (met-cars).[1,2] And it is known that the TMs are important in the synthesis of nanostructures, especially the late 3*d* TMs (Fe, Co, Ni) because of their extensive catalytic and important magnetic properties.[3–8] This fact motivates a study on initial growth processes of the 3*d* TM carbide clusters. In the previous work[9] we discussed in detail the structures and magnetic moments of the FeC_N ($N = 1$–8) and Fe_2C_N ($N = 1$–6) clusters and the influence of the Fe atom(s) on the structures of the C_N ($N = 1$–8) clusters.

So far, data for small cobalt carbide clusters are very limited.[10–13] In order to elucidate clearly the initial growth mechanism, it is essential to investigate the geometric structures of Co–C clusters in the small-size range. In the present work, the geometries, binding energies, and magnetic moments of small CoC_N ($N = 1$–8) and Co_2C_N ($N = 1$–6) clusters are studied systematically using all-electron DFT. The influence on the structures by adding one or two Co atom(s) to small C_N ($N = 1$–8) clusters is also discussed.

2. COMPUTATIONAL DETAILS

The computational method used in this work has been described in detail elsewhere.[14,15] In the electronic structure calculations, we have chosen a double-numerical basis with polarized functions (DNP)[16] basis set and spin unrestricted calculation. First of all, we performed all-electron test calculations on the Co_2 and C_2 dimers using several kinds of exchange-correlation functionals. The results of the test are summarized in Table I. The binding energy of a cluster system is defined as $E_b = E_{tot} - E_{sum}$, where E_{tot} is the total energy of the cluster and E_{sum} is the sum of the energy of all free atoms in the cluster.[17,18]

From Table I, it is obvious that the results obtained using BLYP (the Becke exchange functional[22] and the Lee-Yang-Parr correlation functional[23]) are closest to the experimental data in bond length. It should also be noted that the BLYP functional has been applied successfully in previous calculations.[9,24–27] Therefore, we chose the BLYP exchange-correlation functional together with the DNP basis functions in the present study.

In order to obtain accurate calculations, we chose an octupole scheme for the multipolar expansion of the charge density and coulomb potential. In the optimization, the energy gradient and atomic displacements are converged within 1×10^{-4} Hartree/Bohr and 1×10^{-4} Å, respectively. The charge density in the self-consistent iterations is converged within 1×10^{-6} e/Å^3, which corresponds to a total energy convergence of 1×10^{-5} Hartree. All calculations are performed in the DMol^3 package.[14,28]

3. RESULTS AND DISCUSSION

The typical geometric structures of the low-lying isomers found for CoC_N ($N = 1$–8) clusters are shown in Figure 1;

*Author to whom correspondence should be addressed.

1533-4880/2010/10/5490/005 doi:10.1166/jnn.2010.1957

Table I. Calculated atomic bond lengths a_0 (in Å) and binding energies E_b (in eV) of the Co_2 and C_2 dimers in the ground states.

Cluster	Property	VWN	PW91	BP	BLYP	PBE	Expt.
Co_2	a_0	1.946	2.123	2.127	2.144	2.127	2.31[15, 19]
	E_b	−5.89603	−5.48520	−5.39439	−5.07996	−5.36794	−1.72[15, 19]
C_2	a_0	1.306	1.312	1.315	1.314	1.314	1.31[20, 21]
	E_b	−7.52947	−6.88582	−6.71660	−6.62546	−6.90835	−6.08[20, 21]

the results are summarized in Table II. In the previous work,[9] the all-electron DFT calculations confirm the well-established view[29] that the lowest-energy forms of C_N clusters with $N < 10$ are the linear chains. The ground states of CoC_N (N = 1–8) obtained here are predicted to be linear structures with the Co atom bonded at one end, except in the cases of CoC_2 and CoC_7. For CoC_N (N = 3–8) clusters, the carbon atoms form a continuous chain and no carbon dimers are observed.

For CoC, the binding energy is −5.91714 eV, which is 0.70 eV higher than that of the pure C_2 dimer. The lowest-energy structure of CoC_2 has C_{2v} symmetry, which is in agreement with the previous results.[10] Two kinds of linear structures (C_v and D_h) are also considered. The C_v structure is 0.2307 eV higher in energy than that of the ground state, and is assigned as the second isomer. Analysis of the Mülliken population shows that 0.072e transfers from the Co atom to the C atom in the CoC cluster, 0.286e transfers from the Co atom to the C atoms in the CoC_2 cluster, and that the spin moment, 1 μ_B, lies primarily on the Co atom. In this work, the observation has also been found to exist in other clusters.

In the case of CoC_3, the lowest-energy structure obtained here is the C_v structure with the Co atom at one end. It is in contrast with the result of Wang and Li by a magnetic-bottle photoelectron spectroscopy (PES) apparatus with a laser vaporization cluster source.[13] They indicated that the lowest-energy structure was a C_{2v} ring ($C_{2v}(OR)$ (Oblate rhomboid: OR)) structure, whose energy is 0.285 eV higher than that of the lowest-energy state obtained here. And it is the second stable isomer. The number of bonds in the $3D$ (C_{3v}) structure is largest; however, its binding energy is also highest of all the structures.

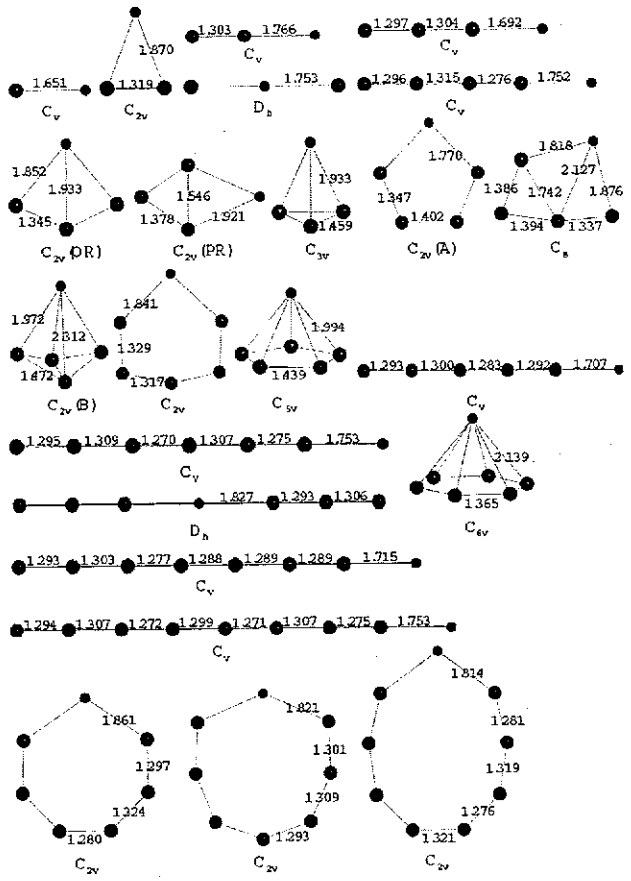

Fig. 1. Various geometric structures for the lowest-energy isomers found for CoC_N (N = 1–8) clusters. The bond lengths (in Å) of the various structures are specified correspondingly. Large spheres represent C atoms, and small spheres, Co atoms.

Table II. Calculated results for various structures of CoC_N (N = 1–8) clusters. The table lists the symmetry (Sym.), binding energy E_b (in eV), HOMO state, the energy difference ΔE between LUMO and HOMO, the electron occupation number n in the HOMO, and the total spin moment μ_s (in μ_B).

Cluster	Sym.	E_b	HOMO	ΔE	n	μ_s
CoC	C_v	−5.91714	A1.1	0.328	1	1
CoC_2	C_{2v}	−12.82341	A1.1	0.607	1	1
	C_v	−12.59269	A1.1	0.636	1	3
	D_h	−8.59395	A2U.1	0.988	1	5
CoC_3	C_v	−19.62610	A1.1	1.186	1	1
	$C_{2v}(OR)$	−19.34131	A1.1	1.145	1	1
	$C_{2v}(PR)$	−18.55855	A1.1	0.988	1	3
	C_{3v}	−17.20370	E.2	1.156	2	3
CoC_4	C_v	−25.89332	A1.1	0.873	1	3
	C_s	−24.80981	A'.1	0.468	1	1
	$C_{2v}(A)$	−24.23295	B1.1	0.725	1	1
	$C_{2v}(B)$	−22.46394	B1.1	0.736	1	3
CoC_5	C_v	−32.82368	A1.1	1.100	1	1
	C_{2v}	−31.45417	B1.1	0.765	1	1
	C_{5v}	−26.74500	E2.2	0.559	2	4
CoC_6	C_v	−39.16010	A1.1	0.774	1	3
	D_h	−36.90216	A1G.1	0.327	1	1
	C_{2v}	−38.56774	A1.1	0.438	1	1
	C_{6v}	−36.36028	E2.2	0.704	2	3
CoC_7	C_v	−46.01402	A1.1	0.906	1	1
	C_{2v}	−46.12946	A1.1	1.123	1	1
CoC_8	C_v	−52.40796	E.2	0.669	2	4
	C_{2v}	−52.02499	A1.1	0.594	1	1

In terms of the geometric structures of CoC_N ($N \geq 4$) clusters, there are very limited data both from theory and experiment. The lowest-energy structures of CoC_N ($N = 4$–8) obtained here are predicted to be linear structures with the Co atom at one end, except for CoC_7. At the same time, two- and three-dimensional geometries are also calculated. For CoC_4, the linear structure has the lowest energy with $\mu_s = 3.0\ \mu_B$. The planar and $3D$ structures are all 1.0 eV higher in energy than that of the linear structure. For CoC_5, the lowest-energy structure is the C_v structure with a singlet HOMO state. Both the planar (C_{2v}) and $3D$ (C_{5v}) structures are also 1.0 eV higher in energy than that of the linear structure. The lowest-energy structure for the CoC_6 cluster is also the linear (C_v) structure with the Co atom at one end. It has a singlet HOMO state and a spin moment, $\mu_s = 3.0\ \mu_B$. The D_h structure with the Co atom at the middle is 2.2579 eV higher in energy than the C_v structure. The planar (C_{2v}) structure with a threefold HOMO state is 0.5923 eV higher in energy than the ground state, and it is the second low-lying isomer. The $3D$ (C_{6v}) structure with a twofold HOMO state has the highest energy, so it is unstable.

From the analysis above, we can see that the binding energies of $3D$ structures are much higher than those of the low-dimension structures. For CoC_7 and CoC_8, we have only selected the linear and the planar configurations. For CoC_7, the C_{2v} structure has the lowest energy and a singlet HOMO state. The linear structure is 0.115 eV higher in energy than that of the ground state, and it is the second low-lying isomer. The lowest-energy structure of the CoC_8 cluster is the linear (C_v) structure. The planar (C_{2v}) structure is 0.383 eV higher in energy than that of the linear structure. The spin moment of the lowest-energy state is $\mu_s = 4\ \mu_B$, however, which is higher than that of the C_{2v} structure: $\mu_s = 1\ \mu_B$. It is difficult to differentiate the stability of C_v and C_{2v}.

Figure 2 shows the geometric structures of the lowest-energy isomers found for Co_2C_N ($N = 1$–6) clusters. The results are summarized in Table III. In all the cases, the lowest-energy structures obtained here have linear geometries with the two Co atoms at the two ends, and the cyclic planar structures are the second low-lying isomers.

For Co_2C, the lowest-energy state is the linear D_h geometry with $\mu_s = 2\ \mu_B$. The planar C_{2v} structure with $\mu_s = 1\ \mu_B$ is 0.5907 eV higher in energy than that of the D_h structure. For Co_2C_2, the stability sequence of considered structures is $D_h < C_s < C_{2v}(A) < D_{2h} < C_{2v}(B)$. And they all have a singlet HOMO state. The planar structures are 0.0370 eV, 0.2201 eV, and 0.8254 eV higher in energy than that of the linear structure, respectively. We consider that D_h and these planar structures are energetic isomers.

For Co_2C_N ($N \geq 3$) clusters, we have also calculated the $3D$ structures and found that the binding energies of these structures are much higher than those of the low-dimension structures. In Figure 2, we only display the linear and the

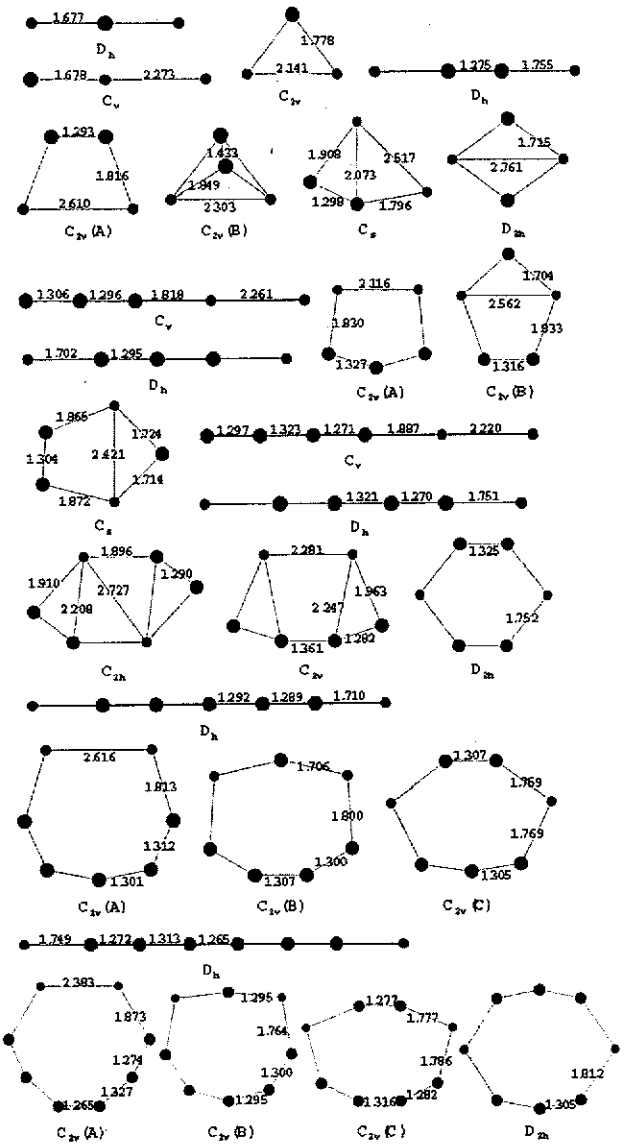

Fig. 2. Various geometric structures for the lowest-energy isomers found for Co_2C_N ($N = 1$–6) clusters. The bond lengths (in Å) of the various structures are specified correspondingly. Large spheres represent C atoms, and small spheres, Co atoms.

planar structures for Co_2C_N ($N = 3$–6) clusters. For Co_2C_3 and Co_2C_4, the difference in energy between D_h and C_v is greater than 1.0 eV. The planar C_s structure is 0.8266 eV higher in energy than that of the ground state for Co_2C_3. In the case of Co_2C_4, the stability decreases in turn from C_{2h}, D_{2h} to C_{2v}. The first one is 0.7376 eV higher in energy than that of the D_h structure.

For Co_2C_5 and Co_2C_6, the lowest-energy structures of them are also the linear D_h structures with the two Co atoms at the two ends. The three planar structures of Co_2C_5 have the similar energies. However, the energy difference between them and the ground state is greater than 1.0 eV. The situation for Co_2C_6 is the same as that of Co_2C_5. The D_{2h} structure has the lowest energy among the four planar

Table III. Calculated results for various structures of Co_2C_N ($N = 1$–6) clusters. The table lists the symmetry, binding energy E_b (in eV), the HOMO state, the energy difference ΔE between the LUMO and HOMO, the electron occupation number n in the HOMO, and the total spin moment μ_s (in μ_B).

Cluster	Sym.	E_b	HOMO	ΔE	n	μ_s
Co_2C	D_h	−10.71259	A2U.1	0.857	1	2
	C_{2v}	−10.12188	A1.1	0.413	1	1
	C_v	−9.00365	A1.1	0.284	2	2
Co_2C_2	D_h	−17.58009	A1G.1	0.720	1	4
	C_s	−17.54313	A'.1	1.104	1	4
	$C_{2v}(A)$	−17.36003	B1.1	1.359	1	4
	$C_{2v}(B)$	−16.35683	B1.1	0.715	1	0
	D_{2h}	−16.75467	B1U.1	0.990	1	0
Co_2C_3	D_h	−24.12761	A2U.1	1.096	1	2
	C_v	−22.57896	E.2	0.460	1	4
	C_s	−23.30101	A'.1	0.518	1	2
	$C_{2v}(A)$	−22.87599	A2.1	0.206	1	2
	$C_{2v}(B)$	−23.16232	B2.1	0.384	1	2
Co_2C_4	D_h	−30.81922	A1G.1	0.679	1	4
	C_{2h}	−30.08163	BU.1	0.922	1	6
	C_v	−28.97852	E.2	0.669	1	4
	D_{2h}	−29.76321	B2G.1	0.623	1	2
	C_{2v}	−29.64880	A1.1	0.456	1	6
Co_2C_5	D_h	−37.36588	A2U.1	0.837	1	2
	$C_{2v}(A)$	−36.01253	A1.1	0.710	1	4
	$C_{2v}(B)$	−36.23145	B1.1	0.727	1	0
	$C_{2v}(C)$	−36.27736	A1.1	0.723	1	0
Co_2C_6	D_h	−44.05825	A1G.1	0.618	1	4
	D_{2h}	−42.99669	B2U.1	0.672	1	2
	$C_{2v}(A)$	−42.59148	A1.1	0.162	1	4
	$C_{2v}(B)$	−42.86421	A2.1	0.951	1	0
	$C_{2v}(C)$	−42.71103	B2.1	0.543	1	3

structures, and is 1.0616 eV higher in energy than that of the linear structure.

It can be seen that the ground states of the CoC_N ($N = 1$–8) and Co_2C_N ($N = 1$–6) clusters are found to be the linear structures except in the case of CoC_2 and CoC_7. For CoC_N ($N = 1$–8) clusters, the ground states are the C_v structures, and the ground states are the D_h structures for Co_2C_N ($N = 1$–6) clusters. The results show that the addition of one Co atom and a second Co atom to small C_N ($N = 1$–8) clusters both leave the linear structures for C_N ($N = 1$–8) clusters almost unaltered. Except for CoC_2, no carbon dimer with clear met-cars characteristic is observed in all the clusters.

4. CONCLUSIONS

In summary, we have obtained the structures, binding energies, and magnetic moments of small CoC_N ($N = 1$–8) and Co_2C_N ($N = 1$–6) clusters using all-electron DFT with the GGA approximation. For the CoC_N ($N = 1$–8) clusters, the ground states are predicted to be the linear (C_v) structures with the Co atom at one end except for CoC_2 and CoC_7. The linear (C_v) and the planar (C_{2v}) structures are computed to be energetically the lowest two isomers for CoC_N ($N = 2$–8). For the Co_2C_N ($N = 1$–6) clusters, the ground states are found to be the D_h structures with the two Co atoms located at the two ends. The planar structures are the second isomer except in the case of Co_2C_5 and Co_2C_6, in which all the planar structures are 1.0 eV higher in energy than the corresponding ground state. In all the cases except in the case of CoC_2, no carbon dimer with clear met-cars characteristics is discovered. For all the clusters, analysis of the Mülliken population shows that charge transfers from the Co atom(s) to the C atoms. The magnetic moment lies primarily on the Co atom(s).

Acknowledgments: We would like to thank Professor Chen Nan-Xian and Professor Shen Jiang for helpful discussions. This work was supported in part by the National Natural Science Foundation of China (Grant No. 10874039 and No. 10747124), and in part by the Natural Science Foundation of Hebei Province (No. 2008000134 and No. A2009000243). We gratefully acknowledge the financial support from the 973 Project in China under Grant No. 2006CB605101.

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Received: 14 September 2007. Revised/Accepted: 2 June 2008.