Density functional theory and reduced density gradient investigations into HCN adsorption on the Co(100) and Co(110) surfaces

Ying-Hu Zhaoa, *, Ying-Yong Wangb, Li Gaoa & Hui Songa

aSchool of Chemical and Environment Engineering, North University of China, Taiyuan 030051, China
Email: tiger5889@126.com

bState Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

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Thirteen kinds of adsorptions of HCN on the Co(100) and Co(110) surfaces at the 1/4 monolayer coverage and the reduced density gradients (RDGs) are investigated using the density functional theory. For Co(100), the adsorption energy of the most stable configuration (where HCN locates at the fourfold site with the C≡N bonded to four Co atoms) is –1.836 eV. On Co(110), the bonding energy in the most favored adsorption configuration (in which HCN locates at the fourfold-long site) is –1.580 eV. The parallel adsorption configuration is energetically favored as compared with the perpendicular mode and the former weakens the strength of C≡N bond to a larger extent than the latter. Thus, the greater activation of the C≡N bond may be found in the parallel configuration and hydrogenation reaction may be easier in the parallel configuration in which the adsorbed HCN becomes non-linear. The binding mechanism of HCN on the Co(100) and Co(110) surfaces is analyzed by Mulliken charge population and the density of states in HCN. The adsorption and metallic-bonding interactions are shown by the low density and low-gradient spike at negative values, while the low density and low-gradient region for the sterically crowded Co atoms remains at positive values indicating repulsion and steric effects.

Keywords: Theoretical chemistry, Density functional calculations, Reduced density gradient, Adsorption, HCN adsorption, Cobalt surfaces

Since adsorption is an inevitable and basic step in heterogeneous catalytic reactions and the catalysts can not speed up the reaction until they can chemically absorb the reactants, the mechanism of catalytic hydrogenation of nitriles is considered to start from the adsorption and dissociation of nitriles on the surface of catalysts, and such a course has already been determined as the reaction rate control step of catalytic hydrogenation of nitriles1,2. Therefore, in order to discover the catalytic mechanism of hydrogenation reaction by nitriles, in recent years, experimental and theoretical studies on the adsorption of HCN, the smallest molecule that contains the nitrile group and usually the model compound of nitriles, on the surface of transition metals have generated considerable interest3–5. Celio et al.3 studied the weak adsorption of HCN on the surface of Ni(111) by reflection absorption infrared spectroscopy (RAIRS). Yang et al.4 investigated the adsorption of HCN on the surface of Ni(111) by using the complete active space self-consistent field method and embedding cluster approach, and obtained results which were partially consistent with the experimental results. Hu et al.5 studied the adsorption and dissociation of HCN on the surface of Cu(100) under the density functional theory (DFT) by means of cluster model, and made theoretical analysis on the experimental results of RAIRS spectra and explored the stability and adsorption energy. The adsorption of HCN on Pt(111) was studied using DFT-GGA calculations and the results were also in good agreement with experimental values6. In 2013, the decomposition mechanism of HCN on Pd(111) was investigated with the DFT-GGA method using the repeated slab model, which was in agreement with the experimental observation, too7.

Many studies have indicated that adsorption pathways, sites and strengths may affect the chemical bond strength and reaction site of reactants in the chemical reactions so as to change the reaction mechanism and therefore cause the change of catalytic activity and selectivity of catalysts8–10. Therefore, many studies have focused on determining whether HCN adsorbs via the lone pair of the nitrogen atom in a perpendicular orientation or parallel to the surface with the C≡N bond. It is reported that HCN adsorbs molecularly on Pd(111) with the C≡N bond parallel to the surface using near-edge X-ray fine structure technique and high-resolution electron
energy loss spectroscopy. Temperature-programmed desorption experiment shows that for the adsorption of HCN on the surface of Pd(111), the low-temperature feature corresponds to the HCN adsorbed via the lone pair of the nitrogen atom in a perpendicular orientation, whereas the high temperature feature is associated with the recombination of atomic hydrogen and CN group. Serafin et al. found that, for the desorption of HCN on W(100), a low-temperature feature associated with HCN adsorbed in a perpendicular orientation, and a high-temperature feature ascribed to HCN adsorbed parallel to the surface. Experiments showed that HCN adsorbs only in a perpendicular orientation for the HCN adsorption on Cu(100) and Pt(111). By the DFT theoretical method, Hu et al. have also found that the top site by the end of N is the optimal adsorption site for the HCN adsorption on Cu(100).

Cobalt is an important transition metal catalyst, and the adsorption and catalytic reactions involving Co have received much attention in recent years. In 2004, Li et al. investigated experimentally the catalytic behavior of Co-B catalyst with the aim to design highly effective catalysts for the CH$_3$CN hydrogenation to C$_2$H$_4$NH$_2$ and discussed the relationship between the catalytic performance and the structural properties of catalyst. An ab initio investigation of the electronic and magnetic structure of Co(001) surface system with hydrogen adsorbed layer has been reported. The relaxed geometries showed that hydrogen had a strong influence on the interlayer distance. Furthermore, a marked reduction of Co surface magnetic moment to 1.41 $\mu_B$ was obtained due to the presence of hydrogen. The preparation of a Mn-promoted Co/TiO$_2$ catalyst for Fischer-Tropsch synthesis was investigated using the strong electrostatic adsorption method for deposition of Mn selectively onto Co to enhance promoter-metal interaction. Benzene adsorption was also studied on metallic cobalt at temperature intervals of 35–85 $^\circ$C and 160–200 $^\circ$C by a chromatographic method.

Recently, several configurations were considered for HCN adsorbed on Co(111) by DFT method. The parallel adsorption modes were found to be energetically favored over the perpendicular ones. The most stable adsorption state for HCN involved two adjacent hcp and fcc 3-fold hollow sites with h-$\eta^5$(N)-f-$\eta^5$(C). Their investigation confirmed the experimental hypothesis about the strong adsorption of the nitrile group on cobalt catalysts, and explained why cobalt-based catalysts were more selective than nickel based catalysts. Tölkes et al. have stated that it is possible to prepare atomically flat Co(110) films and completely remove the oxygen from the Co(110) surface by exposing the surface to atomic hydrogen at 380 K. Co(100) surface is a rather regular low index surface and, similar to Co(111), is also regarded as a large reactive surface. To the best of our knowledge, to date the investigation into the HCN adsorption on the Co surfaces is rather meager, and no theoretical study on the HCN adsorption on the Co(100) or Co(110) surface has been presented.

Density functional theory has been successfully used in the studies on the surface structures and catalytic properties of transition metallic catalysts. In this paper, with the help of DFT and periodic slab model, the configurations of adsorption sites of HCN on the Co(100) and Co(110) surfaces have been optimized. The changes of adsorption energies and structural parameters of HCN on different adsorption sites are discussed, and the charge population and density of states are analyzed. In order to further detect adsorption interactions in real space based on the electron density, the reduced density gradients (RDGs) have been studied. This investigation will have high significance for the further studies on the catalytic mechanism of Co catalysis and the improvement of properties of Co catalyst.

Computational Details

As the crystal structure of metal Co is a face-centered cubic (FCC) structure, considering computational accuracy and efficiency, the 3-layer’s slab was selected to simulate the surface. Initially, the relative positions of the metal atoms were fixed as those in the bulk, with a lattice parameter of 3.52 Å for FCC cobalt according to Oliva et al. (an optimized lattice parameter of 3.5207 Å). It was found that though different numbers of selected layers had a slight impact on the adsorption energy, the geometric configuration of adsorbate and stability order of adsorption sites remained the same. Therefore, the adoption of three metal atomic layers and supercell with surface of 2x2 was feasible.

All calculations were completed by CASTEP module based on DFT in the Materials Studio 4.0 software package. The GGA-PBE method combined by Generalized Gradient Approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functional was used in exchange-correlation potential. The ultrasoft pseudopotential (Ultrasoft) expressed by reciprocal
space was used for the interaction between molecule and metal surface, and the kinetic energy cut-off point of plane wave basis set was 300 eV according to Oliva et al.\textsuperscript{9} The total energy was calculated by self-consistent-field iteration method, the convergence value of the total system energy was $2 \times 10^{-6}$ eV/atom, with stress on each atom lower than 0.05 eV/Å, tolerance shift smaller than $2 \times 10^{-3}$ Å and stress deviation smaller than 0.1 GPa.

The bottom layer was fixed in the optimization course of adsorption state, and the magnetic moment of Co was selected to be 2 $\mu$B (expt. value of Co magnetic moment: 1.72 $\mu$B).\textsuperscript{16} The thickness of intercrystal vacuum layer between neighboring layers was set to be 15 Å so as to ensure that the intercrystalline interaction between neighboring layers was small enough. The bond lengths, bond angles and adsorption heights of adsorbed HCN molecules were optimized, and the adsorption of HCN in the supercells of Co(100) and Co(110) with coverage of 1/4 were calculated. The adsorption energy was calculated as follows:

$$E_{\text{ads}} = E_{\text{HCN/slab}} - (E_{\text{slab}} + E_{\text{HCN}})$$

where, $E_{\text{ads}}$ is the adsorption energy, $E_{\text{HCN/slab}}$ is the total energy of the system when HCN is adsorbed on the surface, $E_{\text{slab}}$ is the surface energy, and $E_{\text{HCN}}$ is the energy of HCN before adsorption.

**Results and Discussion**

**Geometry and adsorption energy of HCN/Co(100) and HCN/Co(110)**

All the adsorption configurations were optimized for the adsorption of HCN molecule on the surface of Co(100) by ways of the C≡N bond perpendicular (N-end adsorption) and parallel to the surface. Five kinds of nonequivalent adsorption sites were found (see Fig. 1). t-$\eta^1$(N) (1) is the top adsorption site with perpendicular orientation, while b-$\eta^2$(N) (2) is the bridge adsorption site with perpendicular orientation. Here, $\eta^m(X)$ refers to X atom interacting with $n$ Co atoms on surface. The fourfold site of the hollow adsorption, fourfold (3), can be regarded as the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Optimized structures of HCN adsorption on the (a) Co(100) and (b) Co(110) surfaces.}
\end{figure}
adsorption with parallel orientation because the difference between the distance of C and Co atoms and that of N and Co atoms is small and $\triangle$HCN is equal to 121.9° (see Table 1). Both b- $\eta^1$(C,N) (4) and b- $\eta^1$(C,N) (5) are bridge adsorption sites with parallel orientation. The former shows that the C≡N bond axes of HCN molecules are parallel to the diagonal of Co(100) surface with its C and N atoms interacting with three neighboring Co atoms, respectively. The C≡N bond axes of the latter are parallel to the Co(100) surface with its C and N atoms interacting with only one Co atom, respectively.

For gas-phase HCN molecule, the C–H and C≡N bond lengths are calculated to be 1.074 and 1.161 Å, respectively, and the bond angle of HCN is 180°, which are respectively coincident with the experimental values\(^26\) of 1.064, 1.156 Å and 180°. Table 1 shows the structural parameters of HCN after HCN is adsorbed on the surface of Co(100). From Table 1, we can see that in the adsorption with perpendicular orientation, there are no evident changes of the H–C bond, but the C≡N bond is stretched by 0.021 or 0.023 Å, with little change in $\angle$H–C–N and slope angle between 0.5 and 1.0°. In the adsorption with parallel orientation, the H–C bond is stretched by 0.016–0.023 Å and C≡N by 0.142–0.161 Å, while the $\angle$H–C–N changes between 38.9° and 58.1°. The structure of HCN changes evidently during adsorption with parallel orientation. Hu et al.\(^27\) have studied the structure of Fe(HCN)$_n^+$ (n = 1–6) at the DFT/UB3LYP/6-31G(2df) level and found that HCN molecules are bonded with Fe$^+$ at the end of N, and the C≡N bonds are strengthened in most configurations with the biggest change of 0.017 Å. In our recent investigation on the adsorption of HCN on the surface of Fe(100), the C≡N bond was found to be stretched by 0.009–0.024 and 0.074–0.156 Å for the perpendicular and parallel orientations, respectively\(^28\).

The variations of C≡N bond length in the adsorption on the Fe(100) surfaces with perpendicular and parallel orientations are lower than those in the corresponding adsorption on the Co(100) surfaces.

Table 1 also shows the adsorption energies $E_{ads}$ of HCN adsorbed on different sites on the Co(100) surface. From Table 1, the order of adsorption energy and stability is: fourfold (3) > b-$\eta^3$(C,N) (4) > b-$\eta^1$(C,N) (5) > t-$\eta^1$(C,N) (1) > b-$\eta^1$(N) (2). The adsorption energies in the parallel orientation are much greater than those in the perpendicular orientation, indicating that the structure of adsorption in the parallel orientation is more stable. The changes in bond lengths of H–C and C≡N are most obvious in fourfold (3) and b-$\eta^3$(C,N) (4) with the biggest adsorption energies of −1.836 and −1.705 eV, revealing that the adsorption on the Co(100) surface are mainly in the ways of fourfold (3) and b-$\eta^3$(C,N) (4). Hu et al.\(^5\) found that the C≡N bond length is also stretched on the bridge and hole sites (by 0.0001 and 0.0002 Å) for HCN/Cu(100); smaller than the change in the bond length of C≡N in HCN/Co(100). The adsorption energies are −0.140 and −0.115 eV, respectively, much lower than the corresponding values in HCN/Co(100). These results show that the adsorption of HCN has more stability on the Co(100) surface than on Cu(100) surface. We have also found that the highest adsorption energy (−1.836 eV) of HCN on the Co(100) surface is weaker than that on Fe(100) (−1.928 eV), although as mentioned above, the variations of C≡N bond length in the adsorption on the Fe(100) surfaces are lower than those in the corresponding adsorption on the Co(100) surfaces. It is noted that the crystal structure of metal Fe is a

<table>
<thead>
<tr>
<th>HCN/Co(100)</th>
<th>$E_{ads}$ (eV)</th>
<th>$d_{H-C}$ (Å)</th>
<th>$d_{C-N}$ (Å)</th>
<th>$d_{C-Co}$ (Å)</th>
<th>$d_{C-Co}$ (Å)</th>
<th>$\angle$HCN (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\perp$ t-$\eta^1$(N) (1)</td>
<td>−0.732 (−0.629)</td>
<td>1.070</td>
<td>1.182</td>
<td>1.711</td>
<td>−</td>
<td>179.0</td>
</tr>
<tr>
<td></td>
<td>−0.783</td>
<td>(1.068)</td>
<td>(1.156)</td>
<td>(1.713)</td>
<td></td>
<td>(172.2)</td>
</tr>
<tr>
<td></td>
<td>−0.560 (−0.521)</td>
<td>1.071</td>
<td>1.184</td>
<td>1.720/1.721</td>
<td>−</td>
<td>179.5</td>
</tr>
<tr>
<td></td>
<td>−0.592</td>
<td>(1.068)</td>
<td>(1.157)</td>
<td>(1.668/1.668)</td>
<td></td>
<td>(178.7)</td>
</tr>
<tr>
<td>$\parallel$ Fourfold (3)</td>
<td>−1.836 (−1.625)</td>
<td>1.097</td>
<td>1.322</td>
<td>1.621/1.624</td>
<td>1.734/1.751</td>
<td>121.9</td>
</tr>
<tr>
<td></td>
<td>−1.928</td>
<td>(1.090)</td>
<td>(1.330)</td>
<td>(1.617/1.617)</td>
<td>(1.728/1.728)</td>
<td>(130.1)</td>
</tr>
<tr>
<td>b-$\eta^3$(C,N) (4)</td>
<td>−1.705</td>
<td>1.095</td>
<td>1.309</td>
<td>1.600/1.763/1.801</td>
<td>1.677/1.811/1.845</td>
<td>125.8</td>
</tr>
<tr>
<td>b-$\eta^1$(C,N) (5)</td>
<td>−1.037</td>
<td>1.090</td>
<td>1.303</td>
<td>1.606</td>
<td></td>
<td>141.1</td>
</tr>
</tbody>
</table>

*The values in parentheses and in bold are at the B3LYP/LANL2DZ(6-31G(2df,2p)) and M06-2X/LANL2DZ(6-31G(2df,2p)) levels, respectively.*
body-centered cubic structure while Co is a face-centered cubic structure. Thus, the interaction between the C≡N bond and the Fe atom in the second layer may occur in HCN/Fe(100), which is perhaps one of the causes of the stronger adsorption on the Fe(100) surface than on the Co(100) surface. However, the larger C≡N bond length in the adsorption on the Co(100) surface than that in the corresponding Fe(100) indicates that the C≡N bond breaks more easily on the Co(100) surface and Co(100) may have stronger catalytic activity than Fe(100).

In order to further verify the correctness of the calculation results, according to the method used by Hu et al., the adsorptions of HCN molecule on the top, bridge and fourfold sites on the surfaces of Co(100) are calculated using the B3LYP and cluster model method with the help of Gaussian 03 program. The interaction energies were also calculated using the M06-2X method by Gaussian 09 program in the structures from the B3LYP method. The surface of Co(100) was simulated by Co_{14} cluster (with nine Co atoms on the surface layer, four atoms on the second layer and one atom on the third layer) with \( C_{4v} \) symmetry. The LANL2DZ pseudopotential basis set proposed by Hay et al. was employed for the Co atoms, while the 6-31G(2df, 2p) basis set with the addition of polarization functions was used for H, C and N atoms (calculated results in Table 1). Table 1 shows that there is a small difference in bond lengths and adsorption energies calculated by the three ways, and the maxima of relative deviation are 3.08% and 18.65%, respectively, which suggests the calculation methods used for the structures to be reliable.

As the Co(110) surface has lower catalytic activity, it has been rarely studied on it in the past. The adsorption with parallel or perpendicular orientation was also examined in the HCN/Co(110) system. Eight kinds of nonequivalent adsorption sites were designed (as in Fig. 1). The adsorption with perpendicular orientation was divided into the top and bridge adsorption which contained long- and short-bridge ones. Adsorption with parallel orientation included hollow adsorption sites (fourfold-long and fourfold-short) and parallel bridge (short-bridge(C, N)¹, long-bridge(C, N)¹, bridge(C, N)² and bridge(C, N)³). This shows that the optimal structures of short-bridge adsorption with perpendicular orientation and long-bridge adsorption with parallel orientation (long-bridge(C, N)³) are identical. The optimized adsorption energies and structural parameters are listed in Table 2.

Table 2 shows that in the adsorption with perpendicular orientation, similar to HCN/Co(100), there is no obvious change in H−C bond in the HCN molecule, but the C≡N bond is stretched by 0.017–0.030 Å, and \( \angle \text{H−C−N} \) changes in the range of 0.8–2.4°. For the adsorption with parallel orientation, the H−C bond is lengthened by 0.008–0.035 Å, the C≡N bond is stretched by 0.061–0.169 Å, and \( \angle \text{H−C−N} \) changes from 37.2° to 60.5°. Similar to the adsorption of HCN on the surface of Co(100), the structure of HCN molecule shows greater change in the adsorption with parallel orientation. From Table 2 and Fig. 1, we can see that the adsorption configuration of long-bridge(C,N)³ (11) has been restructured greatly. N atoms form bonds with a Co atom in the first layer and two neighboring Co atoms in the second layer, while C atom generates a bond with a Co atom in the first layer. The order of adsorption energy and stability is: fourfold-long (8) > short-bridge(C, N)¹ (9) > fourfold-short (10) > long-bridge(C, N)³ (11) > t-η¹(N) (6) >

<table>
<thead>
<tr>
<th>HCN/Co (110)</th>
<th>( E_{\text{ad}} )(eV)</th>
<th>( d_{\text{H−C}} )(Å)</th>
<th>( d_{\text{C−N}} )(Å)</th>
<th>( d_{\text{N−Co}} )(Å)</th>
<th>( d_{\text{C−Co}} )(Å)</th>
<th>( \angle \text{HCN} )(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-η¹(N) (6)</td>
<td>-0.819</td>
<td>1.068</td>
<td>1.178</td>
<td>1.601</td>
<td>-</td>
<td>179.2</td>
</tr>
<tr>
<td>b-η¹(N) (7)</td>
<td>-0.723</td>
<td>1.069</td>
<td>1.191</td>
<td>1.710/1.706</td>
<td>-</td>
<td>177.6</td>
</tr>
<tr>
<td>1 Fourfold-long (8)</td>
<td>-1.580</td>
<td>1.109</td>
<td>1.330</td>
<td>1.643/1.642</td>
<td>1.771/1.762</td>
<td>119.5</td>
</tr>
<tr>
<td>Short-bridge(C,N)¹ (9)</td>
<td>-1.239</td>
<td>1.092</td>
<td>1.258</td>
<td>1.620</td>
<td>1.680</td>
<td>128.7</td>
</tr>
<tr>
<td>Fourfold-short (10)</td>
<td>-1.231</td>
<td>1.103</td>
<td>1.326</td>
<td>1.663/1.663</td>
<td>1.761/1.760</td>
<td>122.6</td>
</tr>
<tr>
<td>Long-bridge(C,N)³ (11)</td>
<td>-1.115</td>
<td>1.100</td>
<td>1.292</td>
<td>1.630/1.728/1.731</td>
<td>1.619</td>
<td>126.3</td>
</tr>
<tr>
<td>Bridge(C,N)² (12)</td>
<td>-0.779</td>
<td>1.082</td>
<td>1.257</td>
<td>1.800/1.801</td>
<td>1.743/1.746</td>
<td>130.5</td>
</tr>
<tr>
<td>Bridge(C,N)¹ (13)</td>
<td>-0.646</td>
<td>1.085</td>
<td>1.222</td>
<td>1.802</td>
<td>1.707</td>
<td>142.8</td>
</tr>
</tbody>
</table>
bridge(C, N)\textsuperscript{3} (12) > b-\eta\textsuperscript{2}(N) (7) > bridge(C, N)\textsuperscript{1} (13). Similar to the Co(100) surface, the energy of adsorption with parallel orientation is much greater than that with perpendicular orientation, which demonstrates that the former structure is more stable. The changes in the H–C and C≡N bond lengths are most evident in fourfold-long (8), with the biggest adsorption energy (−1.580 eV). This result shows that the adsorption on the Co(100) surface is mainly on the fourfold-long (8).

Overall, from Fig. 1 and Tables 1 and 2, we can see that on the surface of Co(100), the optimal adsorption configuration is the fourfold site on the surface where the C≡N bond forms the bond with four neighboring Co atoms. On the surface of Co(110), the most stable adsorption configuration is fourfold-long. Oliva et al.\textsuperscript{9,10} have found in their study on adsorption of HCN/Co(111) that in the adsorption with parallel orientation, the adsorption energy ranges from −0.86 to −1.72 eV, and the order of adsorption energy and stability is: f-\eta\textsuperscript{3}(C)-h-\eta\textsuperscript{3}(N) > f-\eta\textsuperscript{3}(N)-h-\eta\textsuperscript{3}(C) > h-\eta\textsuperscript{3}(C,N) > f-\eta\textsuperscript{3}(C,N) > b-\eta\textsuperscript{1}(C,N). In the adsorption with perpendicular orientation, this value ranges from −0.25 to −0.64 eV, and the order of adsorption energy and stability is: t-\eta\textsuperscript{3}(N) > b-\eta\textsuperscript{2}(N) = f-\eta\textsuperscript{3}(N) > h-\eta\textsuperscript{3}(N).

The most stable adsorption configuration is the adsorption structure f-\eta\textsuperscript{3}(C)-h-\eta\textsuperscript{3}(N) or h-\eta\textsuperscript{3}(N)-f-\eta\textsuperscript{3}(C) in which the C≡N bond is adsorbed on the surface with parallel orientation. The adsorption energy of the most stable state for HCN/Co(111) is close to that of the most stable state for HCN/Co(100) or HCN/Co(110). It is interesting that for the adsorption of HCN/Co(100), HCN/Co(110) and HCN/Co(111), after the HCN molecule is adsorbed by Co, the C≡N bond becomes long, and thus the C≡N bond strength becomes weak. Furthermore, the changes in the adsorption with parallel orientation are greater than those in the adsorption with perpendicular orientation. The adsorption energy and stability in the former are stronger than those in the latter. As mentioned earlier, the adsorption way and site may change the location of chemical bonds which react in the reactants. Moreover, the stronger the adsorption, the greater is the change of lengths of chemical bonds which participate in the chemical reaction, and therefore, it is easier to react and the catalytic activity is stronger. It is thus speculated that greater activation of the C≡N bond might be found for HCN in parallel configurations. Oliva et al.\textsuperscript{9,10} have also confirmed that for the HCN/Co(111) and HCN/Ni(111), the parallel adsorption modes are energetically favored compared with the perpendicular modes and hydrogenation reaction is easier in the parallel adsorption configuration. It is also important to note that HCN molecules are bent in all adsorptions with parallel orientation, which indicates that the adsorption structure of nonlinear bending formed by adsorbing HCN on the surface is beneficial to the hydrogenation reaction.

The adsorption of CO on metal surfaces has been investigated extensively in recent years\textsuperscript{33,34}. For comparison, the type of bonding for the adsorptions of CO on the Co(100) and Co(110) surfaces at the 1/4 monolayer coverage were also investigated using the density functional theory (see Supplementary Data, Tables S1 and S2).

For the adsorption of CO on Co(100), three adsorption sites (top, bridge, and fourfold hollow) were studied. At top and bridge sites, the CO molecule interacts with the surface with the C≡O bond perpendicular to the surface (C-end adsorption), while at fourfold hollow sites two different geometries are found; one with the C≡O bond perpendicular to the surface and a second one with the CO molecule bent over the surface (tilted configuration). In the tilted configuration, the CO molecule interacts with all four Co atoms as in a fourfold hollow site whereas the O atom interacts only with two Co atoms as in a bridge site (f-\eta\textsuperscript{3}(C)-b-\eta\textsuperscript{2}(O)), and an angle between the CO molecular axis and the surface normal of 39.6° is observed. Similar to the adsorption of HCN/Co(100), the adsorption energy of the tilted CO/Co(100) configuration is larger (−2.03 eV) than at the perpendicular (−1.91 eV), top (−0.92 eV) and bridge (−1.20 eV) sites. The CO molecule is activated (in terms of CO bond elongation) in all four adsorption modes. The CO distance at on top, bridge, and fourfold hollow sites when the CO molecule is vertical with respect to the surface is 1.155, 1.202, and 1.277 Å respectively. However, it is in the tilted configuration that the CO molecule is most highly activated with an increase of the CO distance of 0.162 Å (the gas-phase CO bond length is 1.142 Å).

For the CO/Co(110) adsorption, seven kinds of adsorption sites are found: two perpendicular orientations (top (t-\eta\textsuperscript{1}(C) and bridge (b-\eta\textsuperscript{1}(C)) and five parallel orientations including hollow adsorption sites (fourfold-long and fourfold-short) and parallel bridge (tilted short-bridge (b-\eta\textsuperscript{1}(C)-b-\eta\textsuperscript{1}(O)), deep long-bridge (b-\eta\textsuperscript{2}(C)-b-\eta\textsuperscript{2}(O)) and bridge (b-\eta\textsuperscript{2}(C,O)).
For the adsorption with perpendicular orientation, the C≡O bond is stretched by 0.026 Å and 0.033 Å, respectively. In the adsorption with parallel orientation, the C≡O bond is stretched by 0.029−0.197 Å. Similar to the adsorption of CO on the surface of Co(100), the structure of CO molecule shows greater change in the adsorption with parallel orientation. The adsorption configuration of the deep long-bridge (b-η^3(C)-b-η^2(O)) has been restructured greatly. C atoms form bonds with a Co atom in the first layer and two neighboring Co atoms in the second layer, while O atom generates the bond with two Co atoms in the first layer. The order of adsorption energy and stability is: fourfold-long > tilted short-bridge (b-η^3(C)-b-η^1(O)) > fourfold-short > deep long-bridge (b-η^3(C)-b-η^2(O)) > bridge (b-η^2(C)) > top (t-η^1(C)) > bridge (b-η^2(C,O). The adsorption energy in fourfold-long is up to −2.09 eV.

Similar to the adsorption of HCN/Co(110), the adsorption energy of CO/Co(100) with parallel orientation is much greater than that with perpendicular orientation.

Analyses of Mulliken charge and density of state

It has been extensively shown from many experimental and theoretical results that the adsorption of molecule on the surface of metal is accompanied by interatomic charge transfer and change in the surface electronic structure. Therefore, before and after the adsorption of HCN molecules on the Co surfaces, we can get information on the interaction between HCN molecules and Co surface from the analyses of Mulliken charge population and the density of states (DOS) in HCN, and thus further reveal the catalytic mechanism of Co catalysis.

Table 3 lists the Mulliken charges before and after the adsorption of HCN on the crystal surfaces of Co(100) and Co(110). From Table 3, the number of negative charges increase after the adsorption of HCN molecules on the Co crystal surfaces, demonstrating that after adsorption, Co donates electrons and HCN molecules accept them. After HCN molecules are adsorbed on the surface of Co, the negative charge of HCN is increased, which helps the attack of electrophiles, so as to enhance the reactivity of HCN molecules.

Furthermore, the increase in negative charge of HCN is found to be more notable in the configurations with parallel orientation than in those with perpendicular orientation. On the surface of Co(100), the negative charges in HCN shows the largest increase in fourfold (3) and b-η^3(C,N) (4), where Mulliken charges are changed to −0.70 e and −0.79 e. For Co(110), the negative charges in HCN show the largest increase in fourfold-long (8) and fourfold-short (10), with Mulliken charges of −0.79 e and −0.71 e, respectively. Here, we have also obtained the Mulliken charges of f-η^3(N)-h-η^3(C) and h-η^3(N)-f-η^3(C) for HCN/Co(111) (−0.80 e and −0.78 e), which are close to those in fourfold-long (8) and b-η^3(C,N) (4), respectively. The larger the change in charge, stronger is the adsorptive function. Thus, the configurations with the strongest adsorptive function are f-η^3(N)-h-η^3(C), fourfold-long (8), h-η^3(N)-f-η^3(C), b-η^3(C,N) (4), fourfold-short (10) and fourfold (3), which coincide with the results of adsorption energies.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Site</th>
<th>(q_H)</th>
<th>(q_C)</th>
<th>(q_N)</th>
<th>Total (HCN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN/Fe(100)</td>
<td>⊥ t-η^1(N) (1)</td>
<td>0.38</td>
<td>−0.17</td>
<td>−0.35</td>
<td>−0.14</td>
</tr>
<tr>
<td></td>
<td>b-η^2(N) (2)</td>
<td>0.38</td>
<td>−0.21</td>
<td>−0.46</td>
<td>−0.29</td>
</tr>
<tr>
<td></td>
<td>1 Fourfold (3)</td>
<td>0.21</td>
<td>−0.47</td>
<td>−0.44</td>
<td>−0.70</td>
</tr>
<tr>
<td></td>
<td>b-η^3(C,N) (4)</td>
<td>0.21</td>
<td>−0.49</td>
<td>−0.51</td>
<td>−0.79</td>
</tr>
<tr>
<td></td>
<td>b-η^1(C,N) (5)</td>
<td>0.24</td>
<td>−0.33</td>
<td>−0.40</td>
<td>−0.49</td>
</tr>
<tr>
<td>HCN/Fe(110)</td>
<td>⊥ t-η^1(N) (6)</td>
<td>0.38</td>
<td>−0.16</td>
<td>−0.38</td>
<td>−0.16</td>
</tr>
<tr>
<td></td>
<td>b-η^2(N) (7)</td>
<td>0.38</td>
<td>−0.21</td>
<td>−0.49</td>
<td>−0.32</td>
</tr>
<tr>
<td></td>
<td>1 Fourfold-long (8)</td>
<td>0.20</td>
<td>−0.49</td>
<td>−0.48</td>
<td>−0.77</td>
</tr>
<tr>
<td></td>
<td>Short-bridge(C, N)^1 (9)</td>
<td>0.26</td>
<td>−0.34</td>
<td>−0.38</td>
<td>−0.46</td>
</tr>
<tr>
<td></td>
<td>Fourfold-short (10)</td>
<td>0.21</td>
<td>−0.47</td>
<td>−0.45</td>
<td>−0.71</td>
</tr>
<tr>
<td></td>
<td>Long-bridge(C, N)^1 (11)</td>
<td>0.22</td>
<td>−0.42</td>
<td>−0.49</td>
<td>−0.69</td>
</tr>
<tr>
<td></td>
<td>Bridge(C, N)^2 (12)</td>
<td>0.24</td>
<td>−0.44</td>
<td>−0.41</td>
<td>−0.61</td>
</tr>
<tr>
<td></td>
<td>Bridge(C, N)^1 (13)</td>
<td>0.28</td>
<td>−0.33</td>
<td>−0.34</td>
<td>−0.39</td>
</tr>
</tbody>
</table>
Moreover, after adsorption of HCN on the surface of Co, negative charges of both C and N atoms are increased (Table 3), which helps the electrophiles attack the C and N atoms at the same time in the electrophilic addition reaction of unsaturated C≡N bond. This is also why Co could increase the catalytic activity of the hydrogenation for nitriles. Most of the configurations where the negative charges of C and N atoms are increased, are on the sites of f-η^3(N)-h-η^3(C), fourfold-long (8), h-η^3(N)-f-η^3(C), b-η^3(C,N) (4), fourfold-short (10) and fourfold (3). In these six configurations, the charges of the C and N atoms are in the ranges of −0.47 to −0.51 e and −0.44 to −0.52 e, while the charges before adsorption of HCN molecules are only −0.06 e and −0.34 e, respectively.

In order to further analyze the bonding nature of HCN on the surface of Co, the electronic densities of states before and after the adsorption of HCN in 13 configurations are calculated respectively, as shown in Fig. 2. Figure 2 shows that after adsorption, the Fermi levels (E_f) of HCN are shifted left, which illustrates the increase of charge density in HCN after adsorption. This result shows that the transfer of charges from the surface of Co to HCN activates the HCN surface, which is the same as the results obtained by Mulliken charge analysis. After adsorption, the 2π* orbital areas of HCN in different sites are all reduced, showing that the electrons of the 2π* antibonding orbital in HCN are transferred to the HCN bonding orbital. All DOS images of adsorption configurations may show changes in 5σ bonding orbital from smaller sharp peaks before adsorption into bigger broad peaks after adsorption, with the peak locations shifted left. Such a phenomenon illustrates that after adsorption of HCN on the surfaces of Co(100) and Co(110), the negative charges on the surfaces are increased and the activity of the electrophilic addition reaction is enhanced.

Figure 2 also demonstrates that the peak position in 5σ orbital in the adsorption with perpendicular orientation is left to that in adsorption with parallel orientation, indicating that 5σ orbital in the adsorption with parallel orientation has higher energy, more reactive electron which is easy to lose (i.e. higher activity), and thus is easier for electrophilic addition reaction to take place when compared with configuration in the adsorption with perpendicular orientation. Moreover, on the sites of b-η^3(C,N) (4), the 5σ orbital peak shows greater change in area, stronger adsorption function and thus the electrophilic addition reaction occurs by losing electrons more easily. All these are coincident with the above-mentioned structures, adsorption energies and Mulliken charge analysis.

**Analysis of reduced density gradient**

The reduced density gradient (RDG) can be used to reveal the intermolecular, intramolecular and even covalent interactions in real space based on the electron density. It is defined as

\[
\text{RDG} = \frac{1}{2(3\pi^2)^{1/3}} \left[ \frac{\nabla \rho(r)}{\rho(r)^{4/3}} \right]
\]

In order to explore the features associated with small reduced gradients, we examined plots of RDG versus

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Fig. 2—Total density of states of HCN adsorbed on the (a) Co(100) and (b) Co(110) surfaces.
Due to the reduced computational cost, DFT calculations with small basis sets have been recommended over MP2 for practical RDG visualization of interactions\textsuperscript{24}. Therefore, the plots were generated by evaluating the B3LYP/LANL2DZ density using cluster model method (Co\textsubscript{14} cluster with 9 Co atoms on the surface layer, 4 atoms on the second layer and 1 atom on the third layer) and reduced gradients on cuboid grids with a 0.1 au step size. Figure 3 depicts the results of calculated \(t\eta_1^p(N)\) and plotted by the Multiwfn 2.6 suite\textsuperscript{35} and VMD programs\textsuperscript{36}. The RDG results of the other adsorption configurations are similar to that of \(t\eta_1^p(N)\).

According to Johnson \textit{et al.}\textsuperscript{24}, the sign of \(\lambda_2\) (the second eigenvalue of the electron density Hessian matrix) can be used to distinguish the bonded (\(\lambda_2 < 0\)) from non-bonded (\(\lambda_2 > 0\)) interactions. The spikes can be classified to three types a viz., (i) large, negative values of sign (\(\lambda_2\)) indicative of attractive interactions, such as dipole dipole or H-bonding, (ii) large and positive sign (\(\lambda_2\)) indicating nonbonding interaction, such as strong repulsion or steric effect in the ring/cage, and, (iii) values near zero indicating very weak interactions, such as van der Waals interaction.

As can be seen from Fig. 3(a), the plot includes two parts: left (\(\lambda_2 < 0\)) and right (\(\lambda_2 > 0\)). The top left side and right side points (small density and large reduced gradient) correspond to the exponentially decaying tail regions of the density, i.e., far from the nuclei.

Most important for our present consideration is the region of low density and low gradient. For the left side, one spike present at negative value is found in the low density and low gradient region, a signature of noncovalent interaction. It corresponds to the adsorption interaction between HCN and Co. The density values are between \(-0.040\) a.u. and \(-0.035\) a.u., indicating that the adsorption interaction is strong, as is agreement with the result of the adsorption energy. The density values between \(-0.035\) a.u. and \(-0.030\) a.u. (low reduced gradient) show the metallic bonding interactions. The points on the bottom right side (density values of 0.25–0.35 a.u. and low reduced gradient) correspond to the C–H and C≡N covalent bonds or the repulsion and steric effects among the Co atoms of the Co\textsubscript{14} cluster. In a word, Fig. 3(a) shows data for the adsorption and metallic bonding interactions, with the low density, low-gradient spike at negative values indicative of stabilizing interactions. Conversely, the low density, low-gradient region for the sterically crowded Co atoms remains at positive values indicating the repulsion and steric effects.

The interaction regions can also be located by generating RDG isosurface enclosing the corresponding regions in the real molecular space (see Fig. 1 (b)). It was found that the most obvious character is that the red, blue or green extends through the voids of the Co\textsubscript{14} cluster. In particular, the red comes into being a beautiful network through the entire structure. The red isosurface corresponds to the repulsion and steric effects among the Co atoms of the Co\textsubscript{14} cluster. The blue and green isosurface corresponds to the region of low density, low-gradient spike, seen at negative values, indicative of the attractive interactions among the Co atoms, thus forming metallic bonding interactions. For diamonds, Johnson \textit{et al.}\textsuperscript{24} found a low gradient, low-density

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(a) Plots of the RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue (\(\lambda_2\)) and (b) RDG isosurface (\(s = 0.5\)) at the B3LYP/LANL2DZ level.}
\end{figure}
isosurface for a cuboid section of the diamond crystal. The noncovalent surface extends through the voids of the structure, creating a network similar to that of the covalent bonds. For graphite, the low-gradient, low-density isosurface shows areas of nonbonded overlap at the center of the hexagonal rings, i.e., π–π stacking interactions between the graphene sheets. It is expected that the red isosurface in the CO₃₄ cluster is similar to that of diamond, while the blue and green isosurface corresponds to that of graphite.

Conclusions
In this paper, the adsorptions of HCN on Co(100) and Co(110) surfaces are investigated by DFT. For Co(100), the adsorption energy of the most stable configuration, where the HCN locates at the fourfold site with the C≡N bonded to four Co atoms, is ~1.836 eV. On Co(110), the bonding energy in the most favored adsorption configuration, in which HCN locates at the fourfold-long site, is ~1.580 eV. The parallel adsorption configurations are energetically favored compared with the perpendicular modes and weaken the C≡N bond more than the latter. The greater activation of the C≡N bond may be found in parallel configuration and hydrogenation reaction may be easier in the parallel adsorption configuration in which the adsorbed HCN becomes non-linear. Mulliken charge population and the density of states indicate that after adsorption, charge density of HCN is increased, and the C≡N bond is activated, which may accelerate the hydrogenation reaction in the next step. The adsorption and metallic bonding interactions are shown by the low density and low-gradient spike (blue and green) present at negative values, while the low density and low-gradient region in red for the sterically crowded Co atoms remains at positive values indicating the repulsion and steric effects.

Supplementary Data
Supplementary data associated with this article, i.e., Tables S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A (04)459-468_SupplData.pdf.

Acknowledgement
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