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First-principles Periodic Density Functional Study of CO Adsorption on Spinel-type CuCr2O4 (100) Surface

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The catalytic properties of CuCr\textsubscript{2}O\textsubscript{4} with the cubic normal spinel-type structure were discussed by means of studying CO adsorption on the CuCr\textsubscript{2}O\textsubscript{4} (100) surface in the framework of density functional theory. The results of geometry optimization show that CO prefers to adsorb at a Cu site with the adsorption energy of 133.2 kJ/mol. The adsorptions at all sites lead to a decrease in C–O stretching frequency, an increase in C–O bond length and a net positive Mulliken charge for the CO molecule. Population analysis indicates that the charges transfer from the CO molecule to substrate. The density of states for CO molecule before and after adsorption are also computed to discuss the bonding mechanism of CO.

Key words: Density functional theory, CO, Adsorption, CuCr\textsubscript{2}O\textsubscript{4} (100) surface

I. INTRODUCTION

Spinel-type oxides have a remarkable record of applicability and are used in numerous areas, including magnetic materials, ceramics, catalysis, and batteries [1]. In particular, they have excellent catalytic properties for a variety of reactions. Previous studies show that catalysts consisting of CuCr\textsubscript{2}O\textsubscript{2} and CuCr\textsubscript{2}O\textsubscript{4} phases have higher catalytic activity for CO-O\textsubscript{2} reaction [2], and CO-NO reaction can occur on CuCo\textsubscript{2}O\textsubscript{4} [3,4] catalysts and catalysts consisting of CuCr\textsubscript{2}O\textsubscript{2} and CuCr\textsubscript{2}O\textsubscript{4} phases [5]. This signifies the importance of Cu based spinel systems. In recent publications, there is increasing interest in investigating catalytic properties of spinel by studying its adsorption properties [6,7]. Among them, copper dichromium oxide exhibits higher activity. Since it was first studied by Prince in 1957 with neutron powder diffraction method [8], its structure has desired increasing attention. In general, there are different structures at different chemical environment [9] or temperature for many spinel-type oxides [10,11]. For spinel-style oxide CuCr\textsubscript{2}O\textsubscript{4}, at high temperature (about 860 K), it has normal cubic spinel structure (Fd\textsubscript{3}m), whereas at room temperature the structure can be described as a distorted spinel (I-42d, a=6.04 Å, c=7.78 Å) [8] or distorted spinel (I41/amd, a=6.03 Å, c=7.79 Å) using Rietveld refinement of X-ray powder diffraction [12]. De \textit{et al.} has obtained the cubic CuCr\textsubscript{2}O\textsubscript{4} phase at 923 K, lattice parameter a=8.340 Å [13]. Roy and Ghose have prepared cubic CuCr\textsubscript{2}O\textsubscript{4} phase at room temperature with the lattice parameter a=8.364 Å [14]. The normal spinel CuCr\textsubscript{2}O\textsubscript{4}, a p-type semiconductor, is a very versatile catalyst used in hydrogenation and dehydrogenation of methanol [15], the conversion of CO with NO [5], the abatement of NO\textsubscript{2}, H\textsubscript{2}S removal from coal gases [16] and a number of oxidation reactions [2,17].

What is more, the adsorption of CO molecule is of great interest because activation of C–O bond is propitious to CO oxidation, which is related to both fundamental and pollution control studies [18]. The adsorption of CO on the transition metals surface has been studied extensively both experimentally and theoretically [19-25] and in recent years adsorption on spinel oxide has also intrigued researchers [7].

In this study, we discussed the catalytic properties of CuCr\textsubscript{2}O\textsubscript{4} with the cubic normal spinel-type structure by means of studying CO adsorption on the CuCr\textsubscript{2}O\textsubscript{4} (100) surface in the framework of density functional theory. Adsorption configurations at different sites were optimized and the charges of adsorption sites and adsorbed molecules were analyzed. We also computed the density of states for the adsorbed molecule and adsorption sites before and after adsorption, and this report discussed the bonding mechanism of CO for the active Cu sites and Cr sites.

II. COMPUTATION DETAILS AND MODELS

Density functional theory (DFT) and periodic slab model has been used by employing DMol\textsuperscript{3} program package [26-28] and CASTEP program package [29] in Materials Studio (Version 3.1) of Accelrys Inc. It is generally agreed that DFT method can give quite accurate results for geometry optimization and transition states calculations. This approach has been used in our earlier work on Cu\textsubscript{2}O [30], Au [31] and Cu surfaces [32]. Geometries and bonding energies of CO adsorp-
on CuCr$_2$O$_4$ (100) surface were estimated with the DMOl$^3$ code. In this code, the exchange-correlation effects were described by the generalized gradient approximation (GGA) developed by Perdew, Burke and Ernzerhof (PBE) [33-35]. Molecule orbitals were expanded into a double-numerical basis with polarization functions (DNP), whose size is comparable to Gaussian 6-31G**, and usually yields the most reliable results. For C and O atoms in the CO molecule all electron basis set were used, and for the Cu and Cr atoms effective core potentials were used, namely, ion cores of Cu and Cr atoms were treated to be frozen. A Fermi smearing of 0.005 Hartree (Ha) and a real-space cutoff of 4.5 Å were used to improve computational performance. Throughout calculations the spin-polarized approach was used. The k-grid sampling was set to be 4x4x2 in the Brillouin zone. We tested the accuracy using the DFT method with different exchange-correlation functionals to optimize the cell. The results are shown in Table I, which indicates that the cell parameter values calculated by employing GGA-RPBE method agree well with the experimental ones. Therefore, the lattice constants of bulk CuCr$_2$O$_4$ were set to be 8.246 Å. After the optimization of the bulk crystallats, the CuCr$_2$O$_4$ (100) surface (See Fig.1(a)) was built from an optimized bulk CuCr$_2$O$_4$. The CuCr$_2$O$_4$ (100) surface, a triclinic unit cell with the lattice parameters a=b=5.831 Å and c=13.186 Å, was modeled as 1x1 slab with eight atomic layers concerning two CuCr$_2$O$_4$ formula units. We considered four surface adsorption sites, designated as surface Cu and Cr, surface O$_{surf}$ and subsurface O$_{sub}$, and considered C-end and O-end of CO molecule adsorptions for the most active Cu sites. The uppermost four layers of CuCr$_2$O$_4$ (100) surface are composed of one Cu, two Cr, two O$_{surf}$ and two O$_{sub}$ atoms. Only one CO molecule per super cell was adsorbed on the CuCr$_2$O$_4$ (100) surface. We optimized the atomic coordinates of the substrates and adsorbate molecule.

The adsorption energies were calculated by the following equation:

$$E_{ads} = E_{CO} + E_{slab} − E_{system}$$

where $E_{CO}$ is the energy of the free CO molecule, $E_{slab}$ is the total energy of the slab, and $E_{system}$ is the total energy of the adsorbate/slab system. The same Brillouin-zone sampling was used for calculating the energies of the bare slab and the system.

### III. RESULTS AND DISCUSSION

#### A. Calculation for CO molecule

For consistency, calculations for the gas-phase CO have been carried out using the same super cell approach used for the slab studies. In other words, the molecule was isolated in the CuCr$_2$O$_4$ (100) super cell without substrate. The equilibrium C–O bond length was found to be 1.142 Å which differs by 1.2% from the experimental values of 1.128 Å [36]. The vibration frequency of $\nu=2129$ cm$^{-1}$ was determined which was underestimated by 0.7% from the experimental value of 2143 cm$^{-1}$ [37]. This shows that our calculated values are close to experimental data.

#### B. Calculation for CuCr$_2$O$_4$ (100) surface

To further determine the surface relaxation of CuCr$_2$O$_4$ (100) surface, we optimized the perfect sur-

<table>
<thead>
<tr>
<th>Methods</th>
<th>a/Å</th>
</tr>
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<tbody>
<tr>
<td>LDA-CAPZ</td>
<td>8.012</td>
</tr>
<tr>
<td>GGA-RPBE</td>
<td>8.246</td>
</tr>
<tr>
<td>GGA-PW91</td>
<td>8.176</td>
</tr>
<tr>
<td>GGA-PBE</td>
<td>8.180</td>
</tr>
<tr>
<td>Exp.</td>
<td>8.340 [13]</td>
</tr>
<tr>
<td></td>
<td>8.364 [14]</td>
</tr>
</tbody>
</table>

**FIG. 1** CuCr$_2$O$_4$ (100)-1×1 super cell model and four on-top adsorption sites we considered. (a) unrelaxed surface and (b) relaxed surface.
C. Adsorption of CO on CuCr$_2$O$_4$ (100) surface

1. Adsorption geometry, adsorption energy, and frequency

Table III presents the predicted values of adsorption energies, the corresponding geometric parameters and C–O bond stretching vibration frequencies for CO molecule adsorbed at four possible adsorption sites on CuCr$_2$O$_4$ (100) surface. We represent the distance between adsorption sites and the adsorbed molecule with $d_{S-L}$, the C–O bond length after adsorption with $d_{C-O}$ and the angles between the adsorbed molecules and the surface adsorption sites with $\alpha$. The symbol $\nu_{CO}$ denotes the stretching vibration frequency of the C–O bond. The optimized configurations are shown in Fig.2.

The results of geometry optimization show that the Cu site is energetically favorable with the largest adsorption energy 133.2 kJ/mol. This datum is in accordance with the studies [38,39], where the authors suggested Cu$^{2+}$ presented in CuCr$_2$O$_4$ spinel type catalysts are believed to act as active sites for the CO oxidation reaction. As demonstrated in Table III and Fig.2, the C–Cu bond is found to be 1.790 Å, perpendicular to the (100) plane. The C–O bond length is 1.152 Å, elongat-
gies are sound enough to predict selective adsorption for Cr-CO mode. The differences in adsorption energy for Cu-CO mode is more than twice as the one between Cr sites, it is observed that the adsorption energy 57.5 kJ/mol is not as stable as that computed for Cu site. The adsorption energy for Cu-CO mode is more than twice as much as the one for Cr-CO mode. The differences in adsorption energies are sound enough to predict selective adsorption for CO at Cu site. To get insight into the process of CO adsorbed at Cr site transferring to Cu site, the transition state (TS) was searched by means of Complete Linear Synchronous Transit and Quadratic Synchronous Transit (LST/QST) method in Dmol³ program. The initial state (IS) was the geometric configuration of CO molecule adsorbed at Cr site, and the final state (FS) was the one of CO molecule adsorbed at the Cu site. The activation energy was calculated by the equation \( E_a = E_{TS} - E_{IS} \), and the reaction enthalpy by \( \Delta H = E_{FS} - E_{IS} \), respectively. The results show that the energy barrier is 33.5 kJ/mol along with releasing heat 89.6 kJ/mol. This indicates CO adsorbed at a Cr site easily transfers to a Cu site. When approaching the surface, CO adsorbs selectively at Cu sites. The data support the earlier findings [40] showing that closed-shell molecules like CO tend to prefer the low-spin sites.

We also computed CO adsorption on unrelaxed CuCr₂O₄ (100) surface as shown in Table III with corresponding parameters in parentheses. There are similar trends in case of adsorbed distance, C−O bond length and adsorption angle after CO adsorption over unrelaxed CuCr₂O₄ (100) surface through C-down. However, the overestimated adsorption energies for adsorption on relaxed surface have been computed and compared with the values for adsorption on relaxed surface. It indicates the surface relaxation of substrate has a great influence on the adsorption energy. Therefore the surface relaxation effect has been considered in this work.

### 2. Mulliken population analysis

As Table IV presents, it is observed that CO species become polarized with net positive charge for adsorption at four considered sites on the CuCr₂O₄ (100) surface. Obviously, the adsorption causes electrons transferring from adsorbate to substrate. When concentrating on the decreasing charge of adsorption sites and the increasing charge of the CO molecule, it is found that the charge flow primarily takes place between CO molecule and adsorption sites. Comparing adsorption at active

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**Table III: Calculated equilibrium distances, angles, stretching vibration frequencies and the corresponding adsorption energies for CO adsorption on CuCr₂O₄ (100) surface**

<table>
<thead>
<tr>
<th></th>
<th>C-end</th>
<th>O-out</th>
<th>O-sub*</th>
<th>O-end</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{\text{C-L}} / \AA )</td>
<td>1.790 (1.793)</td>
<td>2.075 (2.047)</td>
<td>3.164 (3.019)</td>
<td>3.369 (3.322)</td>
</tr>
<tr>
<td>( d_{\text{C-O}} / \AA )</td>
<td>1.154 (1.154)</td>
<td>1.145 (1.151)</td>
<td>1.141 (1.144)</td>
<td>1.152 (1.154)</td>
</tr>
<tr>
<td>( \alpha /(^\circ) )</td>
<td>180 (180)</td>
<td>180 (173)</td>
<td>115 (112)</td>
<td>152 (151)</td>
</tr>
<tr>
<td>( \nu_{\text{CO}} / \text{cm}^{-1} )</td>
<td>2090 (2087)</td>
<td>2070 (2018)</td>
<td>2119 (2092)</td>
<td>2092 (2086)</td>
</tr>
<tr>
<td>( E_{\text{sub}} / (\text{kJ/mol}) )</td>
<td>133.2 (192.6)</td>
<td>57.5 (80.8)</td>
<td>9.2 (32.7)</td>
<td>128.6 (176)</td>
</tr>
</tbody>
</table>

*a \( d_{\text{C-Cu}}=1.791 \, \AA, \angle \text{OCCu}=180^\circ \) for unrelaxed surface \( d_{\text{C-Cu}}=1.794 \, \AA, \angle \text{OCCu}=180^\circ \). The calculated values from CO adsorption on unrelaxed CuCr₂O₄ (100) surface are listed in parentheses.
Cu sites through C atom and O atom of CO molecule, it is noted that CO species donate more electrons to adsorption sites through C atom than through O atom. This is because the O element has lower negativity and so has difficulty donating electrons to adsorption sites. This is consistent with the fact that CO adsorption at metal sites through C end often are more energetically favorable than through O atom.

3. Density of states analysis and bonding mechanism for the adsorbed system

Further insight into the type of bonding mechanism for CO adsorption at Cu site and Cr site of CuCr$_2$O$_4$ (100) surface can be obtained by analyzing the density of states (DOS) of the adsorbed CO molecule and adsorption sites before and after adsorption. As shown in Fig.3 and Fig.4, the occupied 5σ orbital of free CO is at the Fermi level, where the energy is zero, and the unoccupied 2π* orbital localizes at the above Fermi level. The peak next to the 5σ orbital is 1π band. After adsorption, all bands of the adsorbed CO below the Fermi level become away from the Fermi level and unoccupied 2π* band shifts to be close to the Fermi level. But the 2π* band still lies above the Fermi level, which implies the metal d orbitals do not back donate electrons to 2π* orbital of the CO molecule. After adsorption, it is obvious that the density of states resonances happen between 5σ band and Cu(3d) or Cr(3d) band, and between 1π band and Cu(3d) or Cr(3d) band. The peak of the Cu(3d) and Cr(3d) bands are broaden, in other words, the Cu(3d) and Cr(3d) orbitals are decolized after adsorption. The above facts indicate that the bonding interaction exists between 1π and 5σ bands of CO molecule and Cu(3d) or Cr(3d) orbital. Meanwhile, the Mulliken population analysis illustrates electrons transfer from the CO molecule to the substrate. The results suggest that slightly antibonding 5σ orbitals and strong bonding 1π orbital transfer electrons to metal 3d orbitals of Cu$^{2+}$ and Cr$^{3+}$ for adsorption at Cu sites and Cr sites. As a result, stretching vibration frequencies of the C–O bond are red shifted and C–O bonds are elongated.

IV. CONCLUSION

CO molecule adsorption on spinel-type CuCr$_2$O$_4$ (100) surface considering four possible adsorption sites, designated as surface Cu and Cr, surface O$_{su}$ and subsurface O$_{sub}$, were investigated at the level of density of functional theory. The results show that the adsorption at the Cu site of CuCr$_2$O$_4$ (100) is the most stable and energetically favorable with a larger adsorption energy of 133.2 kJ/mol. The adsorption at surface Cr site is

<table>
<thead>
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<th>TABLE IV The Mulliken population analysis for CO and adsorption sites before and after adsorption</th>
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<tr>
<td></td>
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<tr>
<td>$q(\text{before})$</td>
</tr>
<tr>
<td>$q(\text{after})$</td>
</tr>
<tr>
<td>$\Delta q_C$</td>
</tr>
<tr>
<td>$q_C$</td>
</tr>
<tr>
<td>$q_O$</td>
</tr>
<tr>
<td>$q_{CO}$</td>
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</tbody>
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*$q_{Cu}(\text{after})=0.115$ Å, $\Delta q_{Cu}=-0.251$. For $\Delta q_C$ and $q_{CO}$, “+” symbols represent losing electrons and “−” symbols represent getting electrons.

FIG. 3 The total density of state of CO and Cu sites before (a) and after (b) CO adsorption on Cu sites.

FIG. 4 The total density of state of CO and Cr sites before (a) and after (b) CO adsorption on Cr sites.

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not as favorable as that at Cu site with the adsorption energy 57.5 kJ/mol. We also considered CO adsorbed through O-end at Cu site and found that CO adsorption through O atom is weak and unfavorable corresponding to the adsorption energy 5.7 kJ/mol. The adsorption at all sites lead to a decrease in C–O stretching frequency, an increase in C–O bond length, and a net positive Mulliken charge.

The Mulliken population analysis indicates that charges transfer from the CO molecule to adsorption sites we have considered. Furthermore, to understand the bonding mechanism of CO on CuCr$_2$O$_4$ (100) surface, we analyzed the density of states of the CO molecule and adsorption sites before and after adsorption. Results indicate that 1π and 5σ bands of CO molecule transfer electrons to Cu(3d) or Cr(3d) orbital. Because of the strong bonding character of 1π orbital and the slightly antibonding character of 5σ orbital, the two interactions lead to a decrease of stretching vibration frequency of C–O bond and an increase of C–O bond length.

V. ACKNOWLEDGMENTS

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