Regular article

Adsorption of NH$_3$, NO$_2$ and NO on copper-aluminate catalyst: an ab initio density functional study

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Abstract. Copper–aluminate (Cu–Al$_2$O$_3$) with a spinel structure is an important catalyst in the abatement of pollution by nitrogen oxides (NO$_x$), and its high-temperature phase, CuAl$_2$O$_4$, is considered to be an active component. In general, the Cu^{2+} ion in CuAl$_2$O$_4$ is believed to act as an active site in the NO$_x$ removal process. However, a theoretical description of adsorption on the Cu^{2+} site is still missing. In this study, the interaction of NH$_3$, NO$_2$ and NO molecules with the Cu^{2+} present on the CuAl$_2$O$_4$(100) surface has been investigated by using a periodic density functional approach. The results show that the adsorption of all the molecules on the Cu^{2+} site is energetically favourable, whereas NO is the most strongly bound with the adsorption site. The driving force of the adsorption is interpreted on the basis of charge transfer between the adsorbates and the (100) surface, and key information about the structural and energetic properties is also addressed.

Keywords: Copper aluminate – Density functional calculations – Adsorption – Surface – CuAl$_2$O$_4$

Introduction

Copper–aluminate (Cu–Al$_2$O$_3$) catalyst, with a spinel-type structure, plays an important role in abatement of NO$_x$ [1, 2, 3, 4, 5, 6] and in oxidation of CO [7] and NH$_3$ to N$_2$ [8]. Experimental studies show that Cu–Al$_2$O$_3$ mixed-oxide catalyst calcined at high temperature possesses a CuAl$_2$O$_4$ phase which is a stoichiometric spinel [3, 4, 8] and is more active than the highly dispersed surface and bulk CuO phases [3]. In CuAl$_2$O$_4$, Cu^{2+} ions are highly dispersed in the Al$_2$O$_3$ matrix [4]. Generally it is accepted that the Cu^{2+} ion present in CuAl$_2$O$_4$ acts as an active site in the catalytic reactions [4, 5, 6, 7, 8]. Shimizu and coworkers [4, 5, 6] investigated the CuAl$_2$O$_4$ catalyst for selective catalytic reduction (SCR) of NO with propene (C$_3$H$_6$), and reported that Cu^{2+} ion is the principal active component and plays a crucial role in all the important catalytic steps, and pointed out that the high activity and selectivity of the catalyst is attributed to the Cu^{2+} ion in the Al$_2$O$_3$ matrix. When NH$_3$ is used as the reducing agent, however, there is no effect on NO conversion [2].

The adsorption property is closely related with the nature of the catalysis, and knowledge of adsorbate adsorption may serve as a basis for the development of a comprehensive mechanism for the SCR of NO$_x$. Previous experimental work reported that the SCR reaction with hydrocarbons and/or NH$_3$ led to a number of surface species on Cu–Al$_2$O$_3$ [1]. To the best of our knowledge, however, very little theoretical work has been undertaken in this field.

In the present study, we investigated the adsorption states and energetics of NH$_3$, NO$_2$ and NO molecules on the Cu^{2+} site of the CuAl$_2$O$_4$(100) surface by using an ab initio density functional approach. The calculations mainly serve two purposes: structural and energetic properties of the adsorption systems, and charge transfer between the adsorbate and the catalyst surface, which is important to understand the nature of the adsorption.

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Computational methods and model

The periodic boundary density functional calculations were performed by using DSolid (from MSI) code [9]. For study of adsorption states with respect to transition-metal-oxide catalysts, our earlier studies [10, 11, 12, 13, 14, 15] show that this methodology is

reliable, and can get rid of the restrictions of the cluster approach. In DSolid within the Kohn–Sham formalism [16], one-electron Schrödinger equations are solved at the $k = 0$ wave vector point of the Brillouin zone. A local density functional approximation (LDA) of Vosko–Wilk–Nusair is employed [17]. Typically, the LDA overestimates the energy difference, but it is able to accurately provide the relative order of the adsorption ability that can be reflected by the calculated adsorption energy. Molecular orbitals are expanded into a set of numerical atomic orbitals by a double-numerical basis with polarization functions (DNP). The DNP is comparable in quality to Pople's split-valence 6-31G** basis set and usually yields the most reliable results [18, 19, 20].

The $CuAl_2O_4(100)$ surface is adopted to study the adsorption properties. The (100) surface consists of two $CuAl_2O_4$ formula units, and the lattice constants along both b and c are 8.064 Å (Fig. 1a). The vacuum distance between neighbouring layers is set to 9.80 Å. At such a distance, interaction between layers is tiny. To get a good compromise between accuracy and computational cost, the (100) surface is modeled by a single monolayer. We optimized the atomic coordinates of the adsorption site (Cu^{2+} ion) and the whole adsorbate molecule, whereas the positions of the other surface atoms remained unaltered from those of the fully optimized clean surface.

Results and discussion

$CuAl_2O_4(100)$ surface and adsorbate molecules

As already described, the (100) surface slab with Cu^{2+} ions is created with $b = c = 8.064$ Å, where two formula units of $CuAl_2O_4$ are contained (Fig. 1a). The (100) surface is fully optimized where the calculated b and c are 7.694 and 7.687 Å, respectively. The equilibrium bond length of Cu–O is 1.78 Å, and the corresponding O–Cu–O bond angle is 126.1° as shown in Fig. 1b. Then,
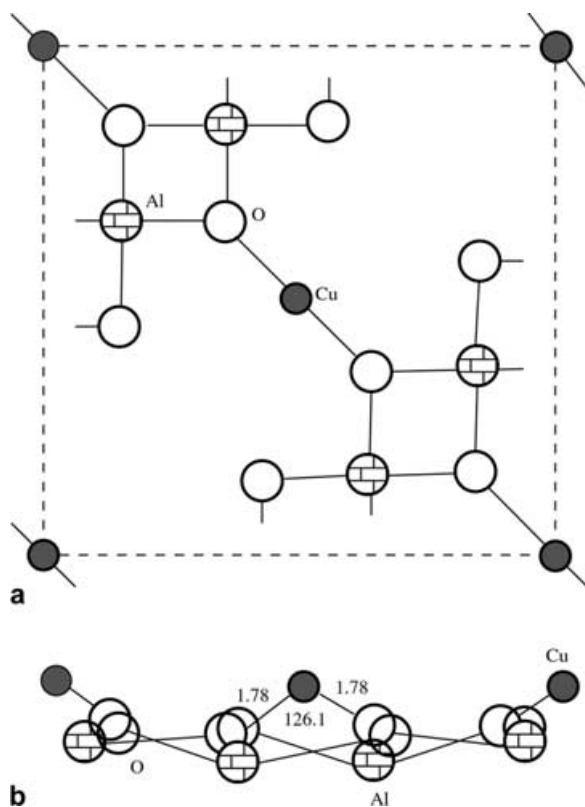
Fig. 1. a Top view of the $CuAl_2O_4(100)$ surface. **b** Side view of the fully relaxed $CuAl_2O_4(100)$ surface

free molecules of NH_3, NO_2 and NO are calculated using a periodic boundary cubic cell with a cell length of 8 Å, and the structural parameters obtained, including the bond length and the bond angle, are listed in Table 1. It shows that our calculated values are in good agreement with experiment data [21].

NH_3 adsorption

When an NH_3 molecule approaches the Cu^{2+} site, adsorption takes place. The adsorption energy is calculated to be -138.6 kcal/mol, indicating a strong interaction between the adsorbate and substrate. As demonstrated in Fig. 2 and Table 2, the N–Cu bond is found to be 2.08 Å, perpendicular to the (100) plane. With NH_3 adsorption, the Cu–O bond was elongated by 0.06 Å, and the O–Cu–O angle changed from 126.1° to 119.6°. In general, when adsorption occurs, the bonding ability in the adsorbate species might be weakened, accordingly the atomic distance might be elongated. This is expected to happen in the case of NH_3 adsorption. Surprisingly, the N–H bond lengths almost remain unchanged. There might be a shortening of the N–H bonds, and such a shortening may be offset by the elongation resulting from the adsorption. When turning to electronic properties, the charges on the N and H atoms are larger than the corresponding charges in free NH_3 (Table 3). The increased atomic charge in the adsorbate species implies that the interaction between the N and H atoms increased correspondingly. As a result, the N–H bond length should be decreased. As expected, this contraction offsets the N–H bond expansion, and the net result shows that the N–H bond length is nearly unaltered.
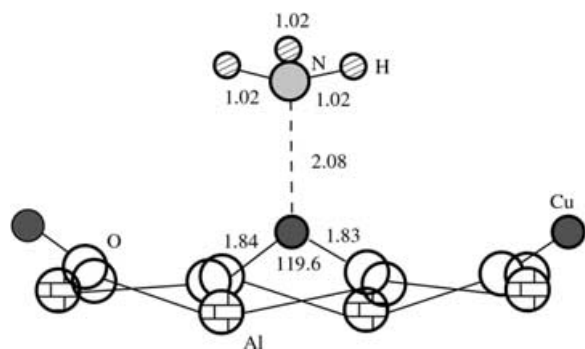
On the other hand, it is observed that the adsorbed NH_3 species is polarized, and has a charge of $+0.177$ (Table 3). This clearly indicates that the adsorbate donated the 0.177 electrons to the substrate. As the adsorption site, as shown in Table 2, the Cu^{2+} decreased its charge by about 0.11, indicating that the Cu^{2+} received about 65% of the electrons donated from the NH_3 species.

NO_2 adsorption

Adsorption of an NO_2 molecule at the Cu^{2+} ion is calculated to be stable energetically, the total energy

Table 1. Calculated bond lengths and/or bond angles of free absorbate molecules

Molecules	Bond length/ angle	Calculated	Experiment [21]
NH_3	$d_{N–H}$ (Å)	1.023	1.012
	∠H–N–H (degrees)	107.1	106.7
NO_2	$D_{N–O}$ (Å)	1.191	1.193
	∠O–N–O (degrees)	133.4	134.1
NO	$d_{N–O}$ (Å)	1.146	1.151

Fig. 2. NH$_3$ adsorption on the Cu^{2+} site of the CuAl$_2$O$_4$(100) surface

Table 3. Atomic charges of the absorbates before and after the adsorption, and net charges of the adsorbate species due to the adsorption

Molecules	Atom/species	Before adsorption	After adsorption
NH$_3$	N	−0.577	−0.608
	H	0.192	0.260
	H	0.192	0.260
	H	0.192	0.265
	NH$_3$	0.000	0.177
NO$_2$	N	0.291	0.290
	O	−0.145	−0.185
	O	−0.145	−0.263
	NO$_2$	0.000	−0.158
ON(–Cu)	N	−0.002	0.094
	O	0.002	−0.021
	NO	0.000	0.073
NO(–Cu)	N	−0.002	0.018
	O	0.002	−0.015
	NO	0.000	0.003

obtained is −127.4 kcal/mol. The distance between the adsorption site and an oxygen of the NO$_2$ is 2.49 Å, as shown in Fig. 3. Owing to the adsorption, the length between the O atom and the N atom is increased by 0.04 Å compared to that in a free molecule, another N–O bond is slightly stretched by 0.01 Å, whereas the bond angle is decreased by 5.3°. However, very little change is observed with respect to the Cu–O bond length and the O–Cu–O angle, as shown in Table 2.

Like the adsorbed NH$_3$, the NO$_2$ species in the adsorption system is also polarized but is negatively charged (−0.158) as shown in Table 3. This clearly shows that charge flow takes place between the adsorbate and the substrate, and the direction of the flow is from the (100) surface to the NO$_2$. Such charge redistribution makes the surface polarized as well. Our previous studies also found that the redistribution property plays a dominant role in adsorption processes [10, 11, 12, 13, 14, 15]. As the adsorption site, the Cu^{2+} ion accumulates about 0.066 electrons in the process as seen in Table 2.

NO adsorption

Owing to the specific bonding property as described in our previous study [13], either the N or the O atom of the NO molecule is able to interact with the Cu^{2+} active site and leads to different bonding configurations (Figs. 4, 5). When the N atom binds with the active site, the calculated adsorption energy of −144.1 kcal/mol shows that the adsorption is favourable energetically. The Cu–N formed bond is 1.75 Å, shorter than that of either NH$_3$ or NO$_2$. At the same time, the Cu–O bond is

elongated by 0.08 Å and the O–Cu–O angle is decreased by 8.7° compared to those before the adsorption owing to the strong interaction between the adsorbate and the active site (Fig. 4).

Regarding the change in the atomic charges, it is observed that the NO species becomes polarized with a net charge of 0.073 (Table 3). Obviously, the adsorption caused a charge flow and the NO donated 0.073 electrons to the substrate and, therefore, the substrate gets polarized as well. Most likely, the majority of the charge is expected to locate at the adsorption site. When concentrating on the charge of the Cu^{2+} ion, however, it is found that the charge on the site decreased by 0.200. This phenomenon shows that this site accumulated not only the charge of 0.073 transferred from the adsorbate, but also the charge of 0.127 (0.200–0.073) from its surrounding atoms within the substrate. This clearly demonstrates that the adsorption process leads not only to the charge transfer from the NO species to the adsorption site, but also to charge flow within the substrate. This process was also observed in our previous adsorption studies [10, 11, 12, 13, 14, 15].

When the O atom of NO interacts with the active site, a stable adsorbate-substrate system is also obtained, and the interaction energy is calculated to be −123.0 kcal/mol (Table 2). This energy is the largest among all

Table 2. Selected structural parameters (bond lengths and bond angles) and atomic charges of the adsorption site as well as adsorption energies with respect to the adsorption of NH$_3$, NO$_2$ and NO on the (100) surface. Note that Δq_{Cu} represents the change in the charge of the Cu^{2+} ion before and after the adsorption

Adsorbates	NH$_3$	NO$_2$	ON(–Cu)	NO(–Cu)	Before adsorption
$d_{Cu-adsorbate}$ (Å)	2.08	2.49	1.75	1.97	–
d_{Cu-O} (Å)	1.84	1.78	1.86	1.78	1.78
∠–O–Cu–O (degrees)	119.6	126.3	117.4	125.8	126.1
q_{Cu}	0.658	0.705	0.571	0.659	0.771
Δq_{Cu}	−0.113	−0.066	−0.200	−0.112	0.000
E_{ads} (kcal/mol)	−138.6	−127.4	−144.1	−123.0	–

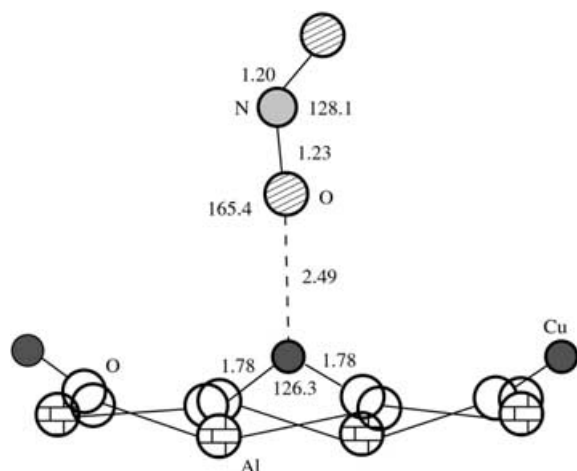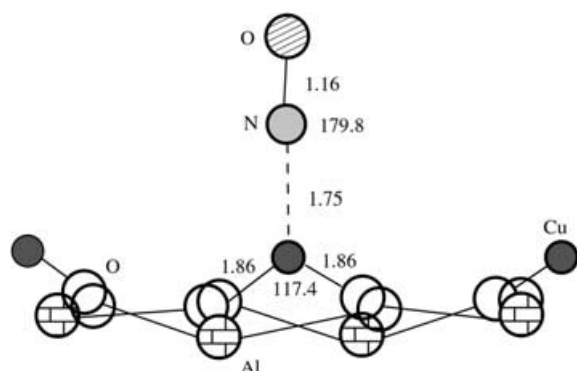**Fig. 3.** NO_2 adsorption on the Cu^{2+} site of the $CuAl_2O_4(100)$ surface

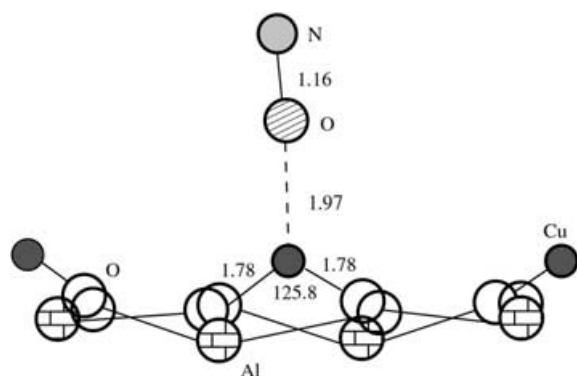**Fig. 4.** NO adsorption by interaction of N with Cu^{2+} on the $CuAl_2O_4(100)$ surface

Fig. 5. NO adsorption through interaction of O with Cu^{2+} on the $CuAl_2O_4(100)$ surface

the cases treated in the current study, which corresponds to the least stability. The newly formed Cu–O bond is 1.97 Å, longer than that of the N–Cu bond for the NO adsorption by 0.22 Å. In the meantime, the change in the Cu–O bond and the O–Cu–O angle is small compared to those before the adsorption (Fig. 5). This is also an indicator of the weak binding between the NO and

the surface through the O and Cu interaction, and is consistent with the calculated adsorption energy. Like the cases already studied, the adsorption site decreased its charge by 0.112 (Table 2), whereas the NO species is almost neutral with a net charge of $+0.003$ (Table 3). This indicates that the decrease of the charge on the Cu^{2+} site is mainly caused by the charge redistribution within the (100) surface.

Comparison of the adsorption states

The adsorption energies demonstrate that all the adsorptions are stable energetically, and the stability decreases in the order $ON(–Cu) > NH_3 > NO_2 > NO$ $(–Cu)$ (Table 2). Like the adsorption on transition-metal oxides such as V_2O_5 and MoO_3 [10, 11, 12, 13, 14, 15], the adsorptions here also resulted from charge transfer between the adsorbate and the substrate, and the direction of the charge flow is from the adsorbate to the (100) surface, except for the NO_2 adsorption with the reverse direction. Eventually, both the adsorbate and the substrate get polarized. The adsorption also leads to relaxation of the adsorption site, and the direction of the relaxation is outward from the surface.

The NO molecule has two different bonding forms to the Cu^{2+} with very different adsorption ability as shown in Table 2. Therefore, only the one with the lower adsorption energy, $ON(–Cu)$, was chosen to compare it with the NH_3 and NO_2 adsorption systems. Table 2 shows that the structural parameters and atomic charges on the active site are correlated well with the adsorption ability. With the decrease in the adsorption ability in the order $ON(–Cu) > NH_3 > NO_2$, the Cu–O bond length in the substrate decreases accordingly, while the atomic distance between the Cu^{2+} and adsorbate, the O–Cu–O bond angle, the atomic charge and increased charge on the active site owing to the adsorption increase correspondingly. All these facts indicate that the change in the geometric and electronic structure induced by the adsorption of NH_3, NO_2 and NO is closely related to the adsorption ability.

Conclusions

Adsorption properties of NH_3, NO_2 and NO molecules on the copper–aluminate surface have been investigated for the first time by using a periodic boundary density functional approach. The results show that the adsorptions of all the molecules on the Cu^{2+} site of $CuAl_2O_4(100)$ are energetically favourable, whereas NO is the most strongly bound with the adsorption site, where the charge transfer between the adsorbates and the (100) surface always takes place and plays an important role during the adsorption processes. The change in the geometric and electronic properties induced by the adsorption of NH_3, NO_2 and NO is correlated well with the adsorption ability. This study might be of help to understand the de-NO_x mechanism and further to design de-NO_x catalysts with excellent performance.

It is hoped that the adsorption properties revealed in this study can serve as a starting point for further studies. Some possible extensions can be the inclusion of the active site into the calculations beyond the single-layer model, and study of the catalytic mechanisms with respect to the NO_x removal over the $CuAl_2O_4$ catalyst.

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