CO and NO adsorption on copper-containing zeolite. A theoretical ab initio study

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Ab initio calculations were performed to simulate the interaction between CO or NO and copper-containing zeolite at the SCF level. The zeolite catalysts were modelled by a molecular cluster of composition $H_8Si_3AlO_4Cu^{\delta+}$ with $\delta = 0, 1$. For $\delta = 0$ the oxidation state of the Cu atom corresponds to 1+ in Cu^+/zeolite, while for $\delta = 1$ it is equal to 2+ in Cu^{2+}/zeolite. It was found that only Cu^+/zeolite should be responsible for CO and NO adsorption from the gas phase. The calculated heats of adsorption compare well with available experimental data and together with adsorption geometries allow us to interpret the observed IR data.

Keywords: CO; NO; Cu/zeolite; ab initio quantum-chemical study

1. Introduction

The role of loaded cations on ion-exchanged zeolites such as Cu/ZSM5, Ce/ZSM5, Ga/ZSM5, Co/ZSM5, Ag/ZSM5, etc. has been the subject of numerous studies during the past decade because of their potential utilization as catalysts for the direct decomposition of NO into N_2 and O_2 [1–12]. Though this direct decomposition of NO into N_2 and O_2 is thermodynamically favorable, it does not occur at low temperature in the absence of a catalyst [13]. At the same time, much attention has also been paid to the decrease of CO and NO concentrations in exhaust gases and to the use of CO as useful resource in chemical industries using metal oxide catalysts [9–12,14,15]. CO adsorption is itself often used as a probe to clarify the loaded cation species and it also modified the coordination geometry around the metal atom in the cluster, for example, on Cu/ZSM5 (see, for example, refs. [9,10]).

Quite recently, Anpo et al. have reported that Cu^{2+} ions supported onto ZSM5 prepared by the ion-exchange method are easily reduced to Cu^+ when the samples are evacuated at temperatures higher than 573 K and that the partially reduced Cu^+ species play a significant role as active species in the catalytic and photocatalytic decomposition of NO [9,10].

The aim of this study consists in the comparison and discussion of the theoretical results concerning the effect of CO and NO adsorption on the local structure of copper ions in the copper-containing zeolites by means of the ab initio method.

2. Computational method and cluster model

In this paper we will model the interaction between CO or NO and the copper-containing zeolite using a molecular cluster of composition $H_8Si_3AlO_4Cu^{\delta+}$ with $\delta = 0, 1$. For $\delta = 0$ the oxidation state of the Cu atom corresponds to 1+ in Cu^+/zeolite, while for $\delta = 1$ it is equal to 2+ in Cu^{2+}/zeolite. Actually, this cluster is a model of the four-membered ring of the zeolite lattice (fig. 1). Ab initio calculations were performed at the SCF level using the GAUSSIAN-92 package [16] with

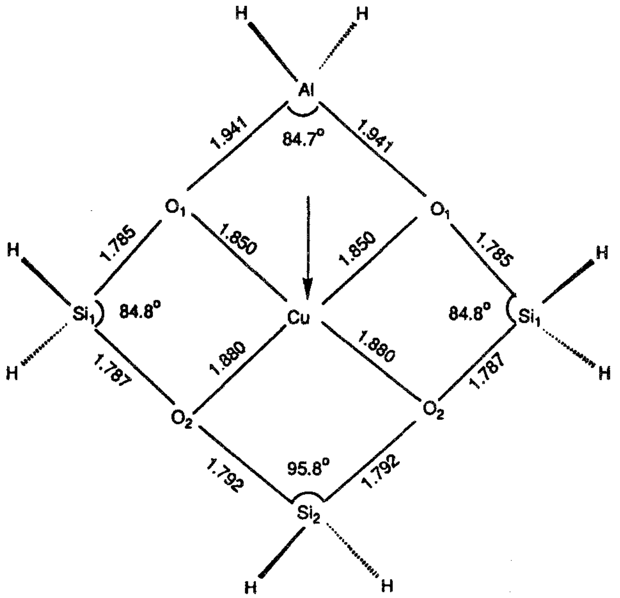

Fig. 1. Cluster model applied to the study of adsorption of CO and NO molecules on the Cu-containing active site of the four-membered ring of the zeolite catalyst. Subscript numbers label the distinct atomic centers. Optimized bond lengths and bond angles for $H_8Si_3AlO_4Cu^+$ are in angströms and degrees, respectively. The arrow indicates the adsorption place for CO and NO.

the so-called LANL1DZ basis set. This notation means that hydrogen atoms that saturate the dangling bonds in the direction to the bulk of the crystal, the carbon, the nitrogen and oxygen atoms are described with a Dunning–Huzinaga valence double-zeta basis set [17], and the aluminium, the copper and silicon atoms with the same double-zeta quality basis set including effective core potentials [18]. The total number of basis functions is 120.

The cluster size is limited by the use of this basis set. Probably the cluster of composition $H_8Si_3AlO_{12}Cu^{\delta+}$, in which eight hydrogen atoms were replaced by eight OH-groups, would be better than the above one. However, as repeatedly shown, the hydrogen atom saturated cluster model is also able to give reliable results and it saves much computational time [19–22]. Note that in the calculations the coordinates of the hydrogen atoms were fixed at the values corresponding to the optimized ones for SiH_4 and AlH_3 molecules at the same basis set, i.e. the Si–H and the Al–H bond lengths were set equal to 1.474 and 1.596 Å, respectively, but the HSiH and HAlH angles were set equal to 109.5°. In the $H_8Si_3AlO_4Cu^+$ cluster the aluminium, oxygen and silicon atoms were put on a plane and their coordinates were optimized using conventional gradient techniques provided that the Cu^{2+} ion is placed at the centre of the four-membered ring. The structure was optimized for the point group C_{2v}. After this optimization step we give some degree of freedom for this Cu^{2+} ion to move out from the planar structure. Then, we considered such a relaxation phenomenon for Cu^+/zeolite, in which the Cu^+ ion is initially placed at the centre of the four-membered ring and then moves to relax. Finally, we considered adsorption of CO and NO molecules on the Cu-containing active site of Cu^{2+}/zeolite and Cu^+/zeolite. In both cases, CO and NO adsorb on the on-top position with C-end and N-end down, respectively. Additional calculations were performed to simulate the interaction of CO with the Cu-containing active site of the zeolite free cluster model.

No counterpoise correction and electron correlation were included in our calculations. Since on-top adsorption of CO and NO was considered throughout this study, we expect that these corrections would be small and do not strongly affect the adsorption energetics of these molecules (see, for example, refs. [19,20]). Heats of adsorption of CO (or NO) were calculated as total energy difference between the adsorption complex and the sum of the isolated initial cluster and CO (or NO).

The open-shell structures were optimized within the UHF method, while the closed-shell structures within the RHF method throughout this study. Since the average value of S^2 is always less than 0.760 for the former structures, a very small increase from the pure doublet value of 0.750 arises from mixing with higher lying quartets, etc.

3. Results and discussion

As is well known, a bridging hydroxyl group in the H-forms of zeolites represents a large local distortion in a pure silica framework [20–22]. This is due to the fact that a proton bonded to one of the basic oxygen atoms of the AlO_4^- tetrahedron makes this Al–O bond length longer than those of the other three and it becomes a donor–acceptor bond. However, for the copper-ion-exchanged zeolite catalyst, the oxygens have an equivalent bond length to the copper atom in the four-membered ring of the zeolite lattice and they become quite symmetrical compared to the Cu atom. This is demonstrated in table 1, in which the results of geometry optimizations of the initial $H_8Si_3AlO_4Cu^+$ cluster, CO and NO adsorption complexes on Cu^{2+}/zeolite and Cu^+/zeolite are summarized. The geometry of CO interacting with the isolated Cu^{2+} and Cu^+ ions, together with those

Table 1
Ab initio optimized geometries (bond lengths, AB (Å) and angles, ABC (deg)) of the initial cluster, some molecules and adsorption complexes

Substrate	Geometry [a]
$H_8Si_3AlO_4Cu^+$ [b]	AlO_1, 1.941; Si_1O_1, 1.785; Si_1O_2, 1.787; Si_2O_2, 1.792; CuO_1, 1.850; CuO_2, 1.880; Si_1Cu, 2.523; Si_2Cu, 2.531; AlCu, 2.743; O_1AlO_1, 84.7; $O_1Si_1O_2$, 84.8; $O_2Si_2O_2$, 95.8
$H_8Si_3AlO_4Cu^+$ [c]	XCu, 0.510; CuO_1, 1.919; CuO_2, 1.948
$H_8Si_3AlO_4Cu$ [d]	XCu, 1.212; CuO_1, 2.212; CuO_2, 2.237
$H_8Si_3AlO_4Cu^+\cdots CO$ [e]	XCu, 1.447; CuO_1, 2.348; CuO_2, 2.372; CuC, 2.133; CO, 1.124
$H_8Si_3AlO_4Cu\cdots CO$ [f]	XCu, 1.271; CuO_1, 2.245; CuO_2, 2.269, CuC, 2.095; CO, 1.129
$H_8Si_3AlO_4Cu^+\cdots NO$ [g]	XCu, 1.037; CuO_1, 2.121; CuO_2, 2.147; CuN, 1.971; NO, 1.077
$H_8Si_3AlO_4Cu^+\cdots NO$ [h]	XCu, 1.248; CuO_1, 2.231; CuO_2, 2.256; CuN, 2.353; NO, 1.200
CO [i]	CO, 1.138
NO [i]	NO, 1.202
NO^- [i]	NO, 1.280
NO^+ [i]	NO, 1.064

[a] Labeling of atoms is given in fig. 1.
[b] Cu^{2+} ion is in the centre of the four-membered zeolite ring.
[c] All coordinates of the atoms are fixed at the values corresponding to case (b) except for the Cu^{2+} ion, for which some possibilities to move out from the zeolite plane are given. X is the initial optimal position of the Cu^{2+} ion in (b).
[d] The same as (c) but for Cu^+/zeolite.
[e] Adsorption of CO on Cu^{2+}/zeolite.
[f] Adsorption of CO on Cu^+/zeolite.
[g] Adsorption of NO on Cu^{2+}/zeolite.
[h] Adsorption of NO on Cu^+/zeolite.
[i] Free gas phase.

Table 2
Heats of CO and NO adsorption

Adsorption complex	ΔE (kcal/mol)
$H_8Si_3AlO_4Cu^+ \cdots CO$	−37.6
$H_8Si_3AlO_4Cu \cdots CO$	11.2
$H_8Si_3AlO_4Cu^+ \cdots NO$	−105.1
$H_8Si_3AlO_4Cu \cdots NO$	5.4
$Cu^{2+} \cdots CO$	48.0
$Cu^+ \cdots CO$	18.6

of free gas phase CO, NO, NO^+ and NO^-, are also given there. Table 2 shows the calculated heats of adsorption (ΔE) of CO and NO on these zeolites and table 3 shows an electron density distribution over the s, p and d orbitals of the Cu atom and effective Mulliken charges on the Cu, C, N and O atoms.

First, we found that Cu^{2+} ion relaxation in Cu^{2+}/zeolite is relatively small and the respective gain in energy amounts to only 1.83 kcal/mol. This means that the Cu^{2+} ion in Cu^{2+}/zeolite exists probably in the square-planar geometry. However, this is not the case in Cu^+/zeolite: the relaxation value amounts to 1.212 Å and is accompanied by an energy stabilization of more than 50 kcal/mol. So, the Cu^+ ion in Cu^+/zeolite is already in a tetragonal pyramidal geometry.

Second, the adsorption of CO and NO proceeds only on Cu^+/zeolite and does not take place on Cu^{2+}/zeolite, in accordance with numerous experimental investigations [8–12]. The calculated heat of CO adsorption on Cu^+/zeolite is quite reasonable and it is in the range of the experimental one for different types of very well characterized metal oxides (see, for example, ref. [23]). The interactions of CO with Cu^+/zeolite and with free gas phase Cu^{2+} and Cu^+ ions are quite different. In the latter case, the higher the charge on the Cu atom the higher the heat of adsorption, while in the former case the charge is redistributed on the whole four-membered ring of Cu^+/zeolite and plays a decisive role on CO interaction with this cluster. The relatively smaller heat of NO adsorption compared to the CO one is also understandable, since it is due to the interaction of an unpaired electron in the nonbonding orbital of NO with an empty s-orbital of Cu^+ in Cu^+/zeolite.

Third, we found that the d-orbital population on the Cu atom is relatively very close to d^{10} for all systems considered, except for gas phase Cu^{2+}/CO, for which it is exactly d^9. Perhaps this might be the reason why the adsorption of CO and NO did not proceed on Cu^{2+}/zeolite. Mulliken analysis shows that a little charge transfer from CO or NO to Cu^+ takes place for the adsorption of CO or NO on Cu^+/zeolite and they are equal to 0.128 and 0.065 e^-, respectively.

Table 3
Electron density distribution over s, p and d orbitals of the Cu atom and effective Mulliken charges on Cu, C, N and O atoms

Complex	Cu atom	Q_{Cu}	Q_C (or Q_N)	Q_O
Cu^{2+}/CO	$s^{0.145}p^{0.077}d^{9.021}$	1.758	0.120	0.123
Cu^+/CO	$s^{0.111}p^{0.074}d^{9.982}$	0.833	0.211	−0.043
Cu^{2+}/zeolite$\cdots$CO	$s^{0.138}p^{0.212}d^{9.952}$	0.698	0.263	−0.118
Cu^+/zeolite$\cdots$CO	$s^{0.165}p^{0.261}d^{9.941}$	0.633	0.288	−0.160
Cu^{2+}/zeolite$\cdots$NO	$s^{0.182}p^{0.311}d^{9.797}$	0.710	0.494	0.281
Cu^+/zeolite$\cdots$NO	$s^{0.117}p^{0.208}d^{9.986}$	0.689	0.214	−0.149

Finally, as mentioned before, CO is a very convenient small adsorbate used as a probe in order to characterize the metal active site. This is particularly the case for infrared (IR) spectroscopy investigations, since the CO stretching vibrational mode ν_{CO} has a sufficiently high extinction coefficient when it adsorbs on metal or metal oxide surfaces. Thus, the CO (or NO) bond length calculated in the adsorption complex on Cu^+/zeolite became shorter than that of free gas phase CO (or NO). This means that the CO bond strength relatively increases under the adsorption process and its ν_{CO} also increases, since there are a lot of both experimental and theoretical direct correlations (see, for example, refs. [23,24]). Perhaps, the absorption band at 2156 cm^{-1} observed in IR measurements [9] should be directly ascribed to the adsorption complex of CO with Cu^+/zeolite. The decrease of this absorption band at 2156 cm^{-1} and the appearance of a new IR absorption band at 2108 cm^{-1} when ^{13}CO is added onto the catalyst with adsorbed ^{12}CO molecules seems a pure isotopical effect. It is well known that the ratio between CO stretching vibrational modes without and with isotopical carbon, i.e. ν_{CO} and $\nu_{^{13}CO}$, satisfies the following simple relationship:

$$\nu_{CO}/\nu_{^{13}CO} = 1.0227\,, \qquad (1)$$

if one takes into account the respective "reduced" masses of ^{13}CO and ^{12}CO. Thus these two bands at 2108 and 2156 cm^{-1} actually originate from one and the same nature and their difference is due to only the isotopical effect of carbon.

It is worth noting that our HF SCF calculations using this Cu-containing zeolite model overestimate this experimental frequency shift of CO ($\Delta\nu_{CO}$) by 43 cm^{-1}. We can only slightly improve this frequency shift ($\Delta\nu_{CO}$ equal to 34 cm^{-1}) using another cluster model of composition $H_{10}SiO_3AlCu$, in which the Cu atom is actually tricoordinated in the zeolite supercage channel. Heat of CO adsorption amounts to only 6.7 kcal/mol for this adsorption complex. This is slightly preferable compared to CO interaction with a bridging hydroxyl group of zeolite, for which the calculated ΔE is equal to 4.8 kcal/mol, and the experimental [25] $\Delta\nu_{CO}$ equal to 32 cm^{-1} is fairly well reproduced by the calculations (36 cm^{-1}).

4. Conclusions

Interactions between CO or NO and copper-containing zeolite were studied within the ab initio quantum-chemical method using a molecular cluster of composition $H_8Si_3AlO_4Cu^{\delta+}$ with $\delta = 0, 1$. For $\delta = 0$ the oxidation state of the Cu atom corresponds to 1+ in Cu^+/zeolite, while for $\delta = 1$ it is equal to 2+ in Cu^{2+}/zeolite.

In accordance with the experimental data, CO and NO adsorption proceed only on Cu^+/zeolite and do not take place on Cu^{2+}/zeolite. Heats of CO and NO adsorption calculated on Cu^+/zeolite are 11.2 and 5.4 kcal/mol, respectively. However, in contrast to the experimental supposition the Cu^+ ion exists in a tetragonal pyramidal geometry in Cu^+/zeolite, while only the Cu^{2+} ion is in the square-planar geometry in Cu^{2+}/zeolite.

The decrease of the IR absorption band at 2156 cm^{-1} and the appearance of a new IR absorption band at 2108 cm^{-1} when ^{13}CO is added onto the catalyst with adsorbed ^{12}CO molecules seems to be a pure isotopical effect, since they are originated from one and the same nature.

Note added in proof

After this paper had been submitted for publication, in addition to dozens of experimental papers a few theoretical papers were reported based on density functional theory (DFT) using very idealized model clusters [26–28]. The description of the similarities and differencies between these studies and the present one will be the subject of a subsequent paper.

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