Vibration frequencies of NCO species as an intermediate for selective reduction of nitrogen monoxide over copper ion-exchanged ZSM-5

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Abstract

Vibration frequencies of the NCO stretching mode were calculated for model molecules of the copper ion-exchanged ZSM-5 catalytic system, $Cu(OH_2)_3X^{n+}$ (X = NCO, NCO^- and HNCO, $n = 1$ or 2) by use of ab initio molecular orbital calculations. The complexes, $Al(OH)_3(NCO)$, $Al(OH)_3(NCO^-)$ and $Al(OH)_3(OCNH)$ were adopted as the models of the zeolite framework. According to the present calculations, the absorption bands observed at 2189 cm^{-1} and 2251 cm^{-1} are assigned to the stretching vibration of the NCO^- coordinating to the copper ion and to the aluminum in the zeolite (ZSM-5) framework, respectively. This result is consistent with the experimental assignment.

Keywords: Nitrogen oxide; Cu-ZSM-5; Ab initio molecular orbital method

1. Introduction

Nitrogen oxides (NO_x) in exhaust gases are one of the main pollutants of air contamination. Much attention, therefore, has been focused on developing new catalysts which can degrade the gas to non-toxic ones such as N_2 or CO_2. Sato and his coworkers found the ion exchanged zeolites to be effective to reduce NO [1]. They also found that Cu-ZSM-5 was one of the best catalysts to reduce NO in the presence of excess O_2 and hydrocarbons [2,3]. Yahiro et al. found an intermediate which reacts with NO to form

N_2 and CO_2 on the catalyst surface [4]. They observed two IR absorptions of 2189 and 2251 cm^{-1} and assigned them to the NCO stretching modes of isocyanate species coordinating to Cu and Al, respectively.

Estimating vibration frequencies in molecular orbital (MO) calculations is a powerful method to investigate observed IR and Raman spectra [5]. It is, of course, impossible to calculate these properties of Cu-ZSM-5 and the intermediates on its surface. However, MO calculations together with the proper choice of model systems enable us to provide an insight into the assignment of the observed absorption bands.

It is considered that unsaturated cupric ions in Cu-ZSM-5 are the active species in the mech-
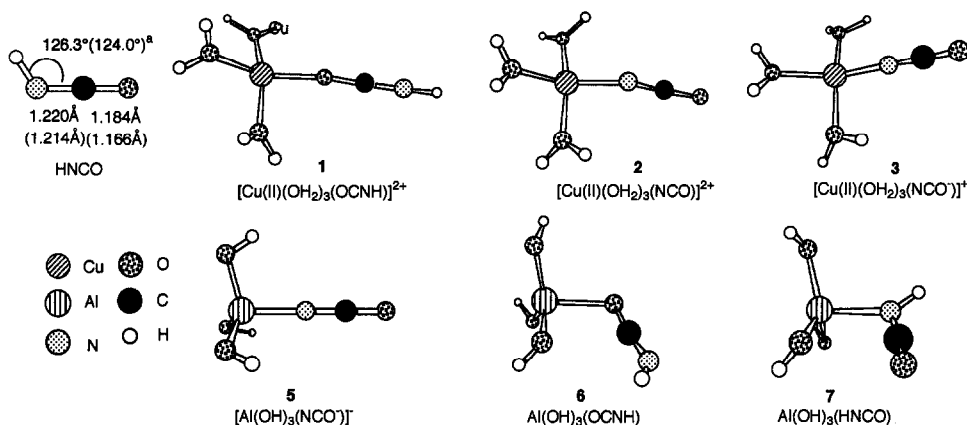
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Fig. 1. Optimized structures of HNCO, the Cu and Al model complexes. [a] Observed values are in parentheses.

anism of nitrogen monoxide decomposition [6]. $Cu(OH_2)_3^{2+}$ was adopted as the model of a Cu site in the Cu-ZSM-5. Kucherov et al. observed that the mixture of NO, C_3H_6 and O_2 gases does not affect the equilibrium oxidation state of the copper in the Cu-ZSM-5 [7]. The NCO radical is also one of the candidates for the NCO species in the catalytic system. In the present study, therefore, we calculated the model complexes with the NCO fragment such as $[Cu(II)(OH_2)_3(OCNH)]^{2+}$ **1**, $[Cu(II)(OH_2)_3(NCO)]^{2+}$ **2** and $[Cu(II)(OH_2)_3(NCO^-)]^+$ **3**. They are the Cu complexes with HNCO, NCO radical and NCO$^-$ fragments, respectively. $Al(OH)_3$ was adopted

as the model of the adsorption sites in the zeolite framework [8]. $Al(OH)_3(NCO)$ **4**, $Al(OH)_3(NCO^-)$ **5**, $Al(OH)_3(OCNH)$ **6** and $Al(OH)_3(HNCO)$ **7** were the models for the NCO species on the zeolite surface. Vibrational frequencies were calculated for the Cu and Al complexes after their geometry optimization in order to assign the observed IR bands in the Cu-ZSM-5 zeolite.

2. Method of calculations

All the calculations were carried out using the GAUSSIAN90 program [9] for the Fujitsu

Table 1
Geometrical parameters (lengths in Å and angles in degree), vibration frequencies (in cm^{-1}) and total energies (in hartree) obtained for isocyanate species in the model complexes

	N–C	C–O	M–N(O)	O–X–O–O [a]	ν	$\nu * 0.95$	Energies
HNCO	1.220	1.184			2390	2271	−167.67024
NCO$^-$	1.210	1.241			2227	2116	−167.56440
NCO	1.253	1.166			2509	2384	−167.55594
1	1.169	1.216	1.897	153.4	2518	2392	−2031.91247
2	1.238	1.186	1.916	154.6	1931	1834	−2031.23258
2′ [b]	1.240	1.180	1.767	−	2093	1988	−2031.16088
3	1.214	1.192	1.824	152.8	2415	2294	−2031.71152
5	1.202	1.210	1.921	131.3	2379	2260	−636.78117
6	1.200	1.204	2.079	152.3	2389	2269	−637.26028
7	1.167	1.249	2.078	150.5	2367	2249	−637.27139

[a] The O–X–O–O is the dihedral angle around the metal atom in $Cu(OH_2)_3$ and $Al(OH)_3$ fragments. X = Cu and Al for Cu and Al complexes, respectively.
[b] 2′ is the optimized geometry of $[Cu(II)(OH_2)_3(NCO)]^{2+}$ in which the Cu atom is forced to have a square planar environment.

S/4IX and the GAUSSIAN92 program [10] for the IBM RS/6000. The geometries of model molecules were fully optimized with the energy gradient method of the Møller–Plesset correlation energy correction at the second order (MP2) level [11]. The 6-31G* basis sets [12,13] were used for all the ligand atoms. The [4s3p2d] contracted basis set was used for copper atoms [14,15], and modified according to the procedure of Kitaura et al. [16].

Fig. 1 displays all the optimized structures of model compounds together with that of HNCO observed [17]. The $\angle$HNC angle was calculated to be 126.3° which is almost equal to the observed value of 124.0°. The calculated N–C, C–O lengths (1.220 and 1.184 Å, respectively) differ only by 0.006 and 0.018 Å from those observed.

The calculations even at the MP2 level systematically overestimate vibration frequencies by about 5% [18]. Therefore, the calculated frequencies at the MP2 level were scaled by a factor of 0.95 in order to have better agreement of the calculated frequencies with the observed ones. In fact, the NCO stretching frequency ν_{NCO} was calculated to be 2271 cm^{-1} which is very close to the observed value 2274 cm^{-1} [17].

3. Results and discussion

Table 1 summarizes the optimized geometrical parameters and their vibration frequencies. The Cu–O length in 1 with the HNCO fragment was calculated to be 1.897 Å. It is interesting to note that the HNC moiety is almost linear in the complex ($\angle$HNC = 177.0°) although the HNCO angle is 126.3° in the free HNCO. While the O atom of the NCO radical was ascertained not to coordinate to $Cu(OH_2)_3^{2+}$, the N atom forms a bond with the Cu whose length turned out to be 1.916 Å in 2. In the optimized structure of 3, the NCO$^-$ coordinates to the Cu of the model active site using the N atom and the Cu–N length was calculated to be 1.824 Å. In the

optimized geometries shown in Fig. 1, all the Cu atoms have basically square planar environment although they tetrahedrally distort a little.

The calculated frequencies of 1, 2 and 3 are 2392, 1834 and 2294 cm^{-1}, respectively. While the calculated values of 1 and 3 are larger by 203 and 105 cm^{-1} than the observed value, that of 2 is smaller by 355 cm^{-1}. A larger ν_{NCO} frequency (1988 cm^{-1}) was obtained for the complex 2' whose geometry was optimized with forcing the Cu atom to have a square planar environment. The ν_{NCO} is largely dependent on the geometry. However, these values are not consistent with the value (2189 cm^{-1}) obtained in the Cu-ZSM-5.

Recently, Kucherov et al. observed in situ ESR spectra of Cu-ZSM-5 in a simulated exhaust gas and found that the concentrations of Cu^{2+} in Cu-ZSM-5 were not changed before and after the gas treatment [7]. We obtained the best agreement between theory and experiment in 3. It is better to assign the 2189 cm^{-1} absorption to the NCO stretching mode which comes from the coordinated NCO$^-$ to the Cu catalyst.

Fig. 1 also displays the optimized structures as the models of isocyanate species on the zeolite framework. It was ascertained in the UHF level calculations that neither the N nor the O atom of the NCO radical coordinates to $Al(OH)_3$. The MP2/6-31G* level theory did not give the optimized structure of the N-coordinated Al complex 4, either. Therefore, we cannot assign the 2551 cm^{-1} absorption to the vibration originating from the NCO radical coordination. The other complexes have reasonable Al–N or Al–O lengths in their optimized structures in 5, 6 and 7. The Al atom of 5 has a tetrahedral environment because the O–Al–O–O angle is 131.3°. On the other hand, 6 and 7 take almost trigonal pyramid geometries.

The calculated ν_{NCO} frequencies are 2260, 2269 and 2249 cm^{-1} for 5, 6 and 7, respectively. The third value is close to that observed (2251 cm^{-1}). However, we have to remember that even in the MP2/6-31G* level theory

there is still a rms error of 61 cm^{-1} [18]. The ν_{NCO} for **5**, which differs by only 9 cm^{-1} from the observed value, should be another candidate for the observed band. We could not expect the formation of HNCO in the catalytic system. It is concluded that the observed frequency is assigned to the ν_{NCO} originating from the NCO anion coordinating to the Al atom in the zeolite framework.

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