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Theoretical study of NO decomposition on Cu-ZSM-5 catalyst models

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Abstract

The decomposition mechanism of NO on Cu-ZSM-5 catalyst models was investigated using ab initio molecular orbital calculations with Huzinaga's MIDI-P basis set [see S. Huzinaga, Gaussian Basic Sets for Molecular Calculations, Elsevier, Amsterdam, 1984]. Two reaction routes were assumed for each model and the geometry of all molecules was optimized.

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1. Introduction

Metal ion-exchanged zeolites, such as Cu-ZSM-5, are reported to show certain activities for decomposition of NO. However, to put these catalysts into practical use, significant improvement in activity is needed. This study is focused on investigating the decomposition mechanism of NO on Cu-ZSM-5. Monodentate catalyst models shown in Fig. 1 were studied and two reaction routes shown in Fig. 2 were considered.

Model 1 is isolated copper ion and model 2 includes the minimum zeolite skeleton as an $Al(OH)_4^-$. The nitrogen atom faces the copper atom of the catalyst, when NO is adsorbed on the catalyst according to route 1. On the other hand, the oxygen atom faces the copper atom in route 2. The common view suggests that NO is adsorbed in I-a structure and the decomposition progresses via route 1. However, that view is based on the general structure of transition metal complexes, and is not supported by any data observed on the Cu-ZSM-5 system directly. Since it is very difficult to distinguish between I-a and I-b experimentally, it is very useful to evaluate the energy and the possibility of each reaction steps in both routes.

1.1. Computational method

All calculations were performed in HF level using the GAUSSIAN92 program [2] with Huzinaga's MIDI-P basis set (Cu: 53321/521/41, N:

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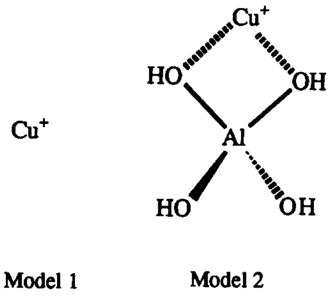


Fig. 1. Catalyst models investigated.

521/41/1, O of NO: 521/41/1, Al: 5321/521, O: 521/41, H: 41) on a Kubota Titan 2-800 workstation, a DEC 3000-800 workstation and a Fujitsu VPX210/10 super-computer. The scale factor of the *d* orbital is 1.0 for N atom and O atom of NO molecule. The geometry of model 2 was optimized keeping C_{2v} symmetry, and used as a fixed structure of the catalyst model on the geometry optimization of I-a, I-b, II-a and II-b. Single point calculations of the MP4 level were carried out for I-a and I-b optimized geometry to confirm the energy difference of both structures more correctly.

2. Results and discussion

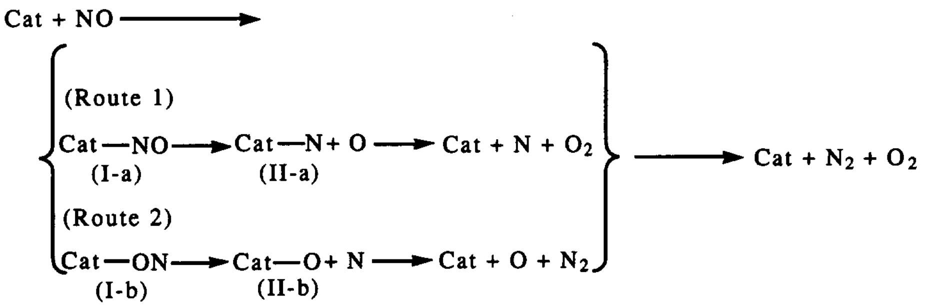
The optimized structure of model 2 and the adsorbed model (I-a, I-b, II-a and II-b) are shown in Figs. 3 and 4. Energy changes via each route are shown in Figs. 5 and 6. Deviations of S^2 from the theoretical value were within 0.025 before annihilation in all calculations.

2.1. NO adsorption on the catalyst models

The results of the calculations are summarized in Tables 1 and 2. The differences of adsorption energy between the I-a and I-b structure are very small, e.g. 2.45 kcal/mol in model 1 and 2.21 kcal/mol in model 2 at HF level, and the relative energy between these two structures is changeable by calculation level such as HF or MP4. This suggests that the adsorption energy of both is nearly equal, and NO can be adsorbed equally in the I-a and I-b structure.

The distance between the Cu atom and the NO molecule is more than 2.19 Å and the bond length of NO scarcely varies from that of free NO. Other properties such as atomic charges and atomic spin densities do not show significant change by adsorption. These results indicate that the electronic interaction between the NO molecule and the catalyst models is not found in this adsorption state. Therefore, the adsorption is similar to physisorption rather than chemisorption.

The observed IR spectrum of NO on Cu-ZSM-5 shifts to a lower frequency than the spectrum of free NO [3]. Although this frequency shift is caused by the extension of the NO bond length



Cat : Cu^+ (model 1), $Cu^+[Al(OH)_4]^-$ (model 2)

Fig. 2. Two reaction routes assumed in this study.

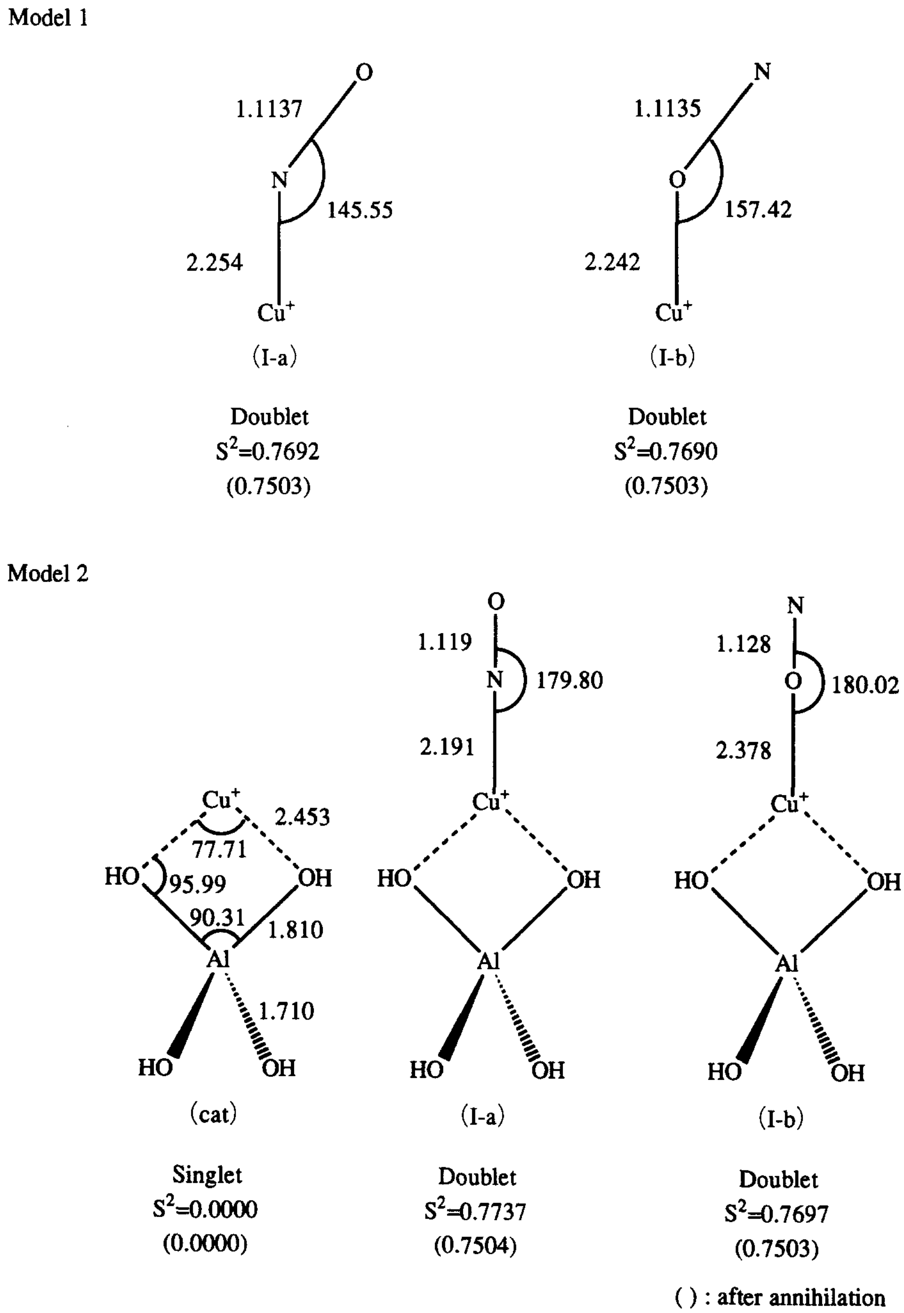
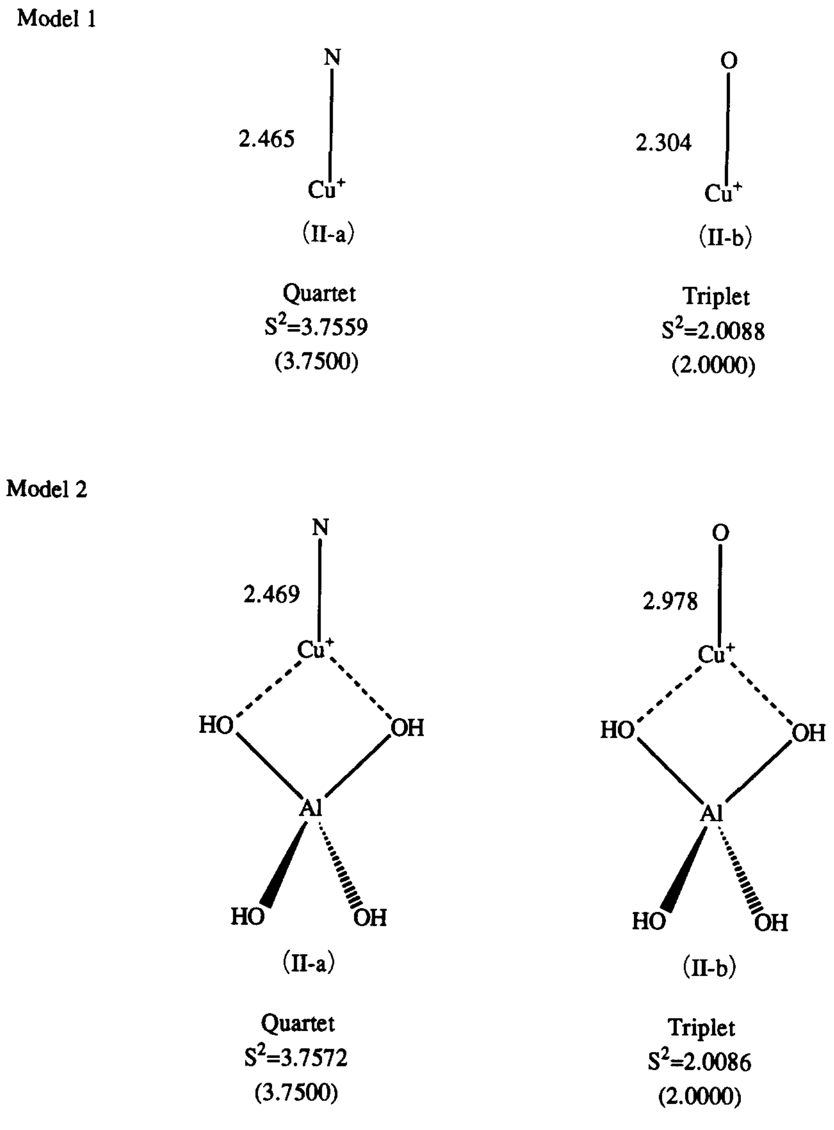


Fig. 3. Optimized geometries of NO adsorbed model. Bond lengths are given in Å and bond angles in degrees.

with electron transfer from Cu^+ to NO, our calculations have not yet represented this state (Table 3).

2.2. NO decomposition reaction

The NO decomposition reaction follows the adsorption step, and the energy changes from I to II are 104.10 kcal/mol (model 1, route 1), 97.21 kcal/mol (model 1, route 2), 100.94 kcal/mol (model 2, route 1) and 91.33 kcal/mol (model 2, route 2), respectively. These results explain the experimental result that the decomposition of adsorbed NO occurs at high temperatures (400–500°C). Comparison of the results between the



( ) : after annihilation

Fig. 4. Optimized geometries of N or O atom adsorption model. Bond lengths are given in Å and bond angles in degrees.

two models shows that the zeolite skeleton contributes somewhat to decreasing the enthalpy for decomposition of NO adsorbed on the catalyst.

In both cases of the two models, it is expected that the reaction of route 2 occurs more easily than the reaction of route 1, because the energy barrier of route 2 is smaller than route 1 and the formation energy of N_2 from two nitrogen atoms (-104.80 kcal/mol) is quite effective in continuing the reaction (Figs. 5 and 6). This result is contrary to the common view of the transition metal complex. However, the observation of the interaction between NO and Cu is very difficult, since the vibrational frequency of Cu–O or Cu–N is too low to measure the spectrum (calculated value is 115 cm^{-1} for Cu–N and 91 cm^{-1} for Cu–O, respectively).

The desorption energy of atomic oxygen adsorbed on the copper atom is larger than that of nitrogen. This indicates that the reaction of route

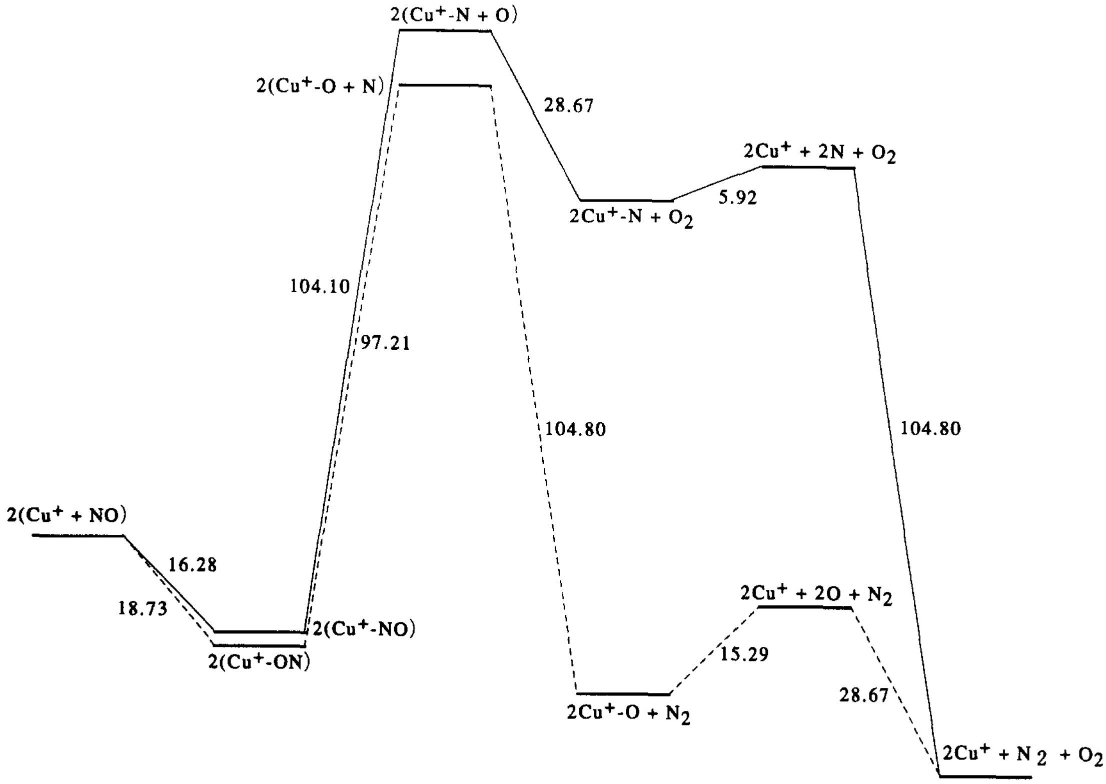


Fig. 5. Schematic energy profile for NO adsorption and decomposition on catalyst model 1. Energies are given in kcal/mol.

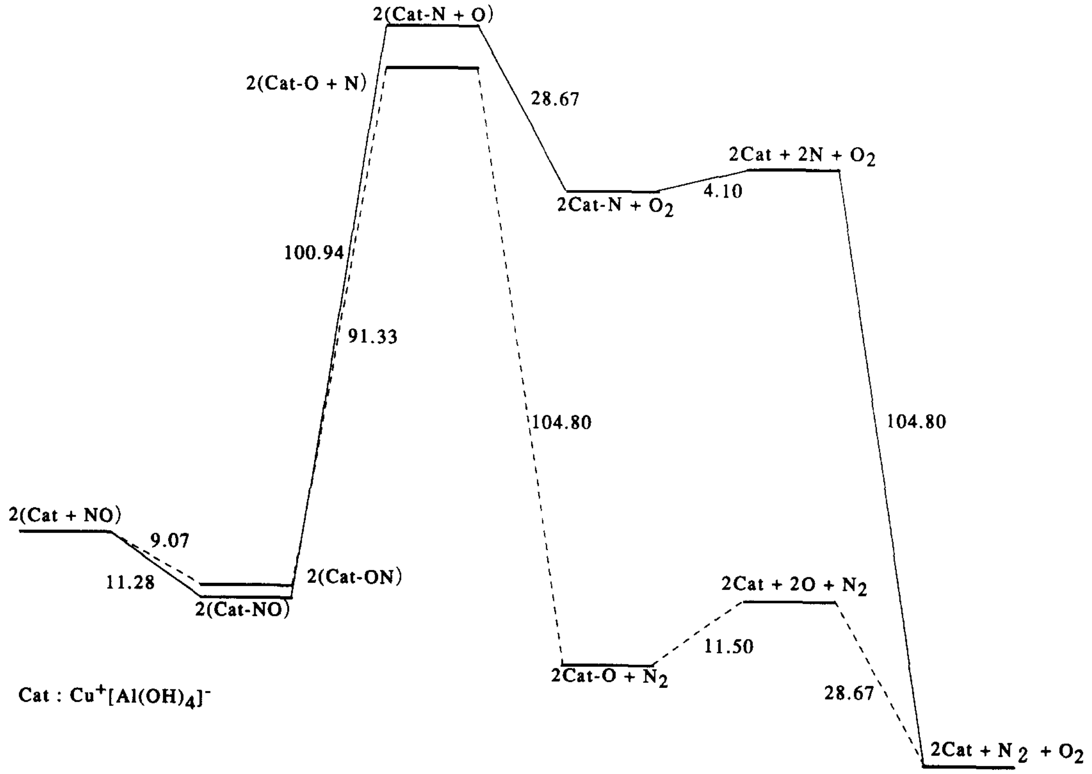


Fig. 6. Schematic energy profile for NO adsorption and decomposition on catalyst model 2. Energies are given in kcal/mol.

Table 1
Atomic properties resulting from the calculations using catalyst model 1

	Model 1	NO	I-a	I-b	II-a	II-b
Bond length (Å)						
Cu–O	–	–	–	2.242	–	2.304
Cu–N	–	–	2.254	–	2.465	–
N–O	–	1.126	1.114	1.135	–	–
Atomic charge						
Cu	1.0000	–	0.9643	0.9807	0.9805	0.9622
N	–	0.0952	−0.0102	0.2559	0.0195	–
O	–	−0.0952	0.0459	−0.2366	–	0.0378
Atomic spin density						
Cu	0.0000	–	0.0107	0.0020	0.0122	−0.0126
N	–	0.8470	0.7721	0.9038	2.9878	–
O	–	0.1530	0.2172	0.0942	–	2.0126
HF energy (a.u.)	−1638.2444	−129.2421	−1767.4994	−1767.5014	−1692.6310	−1713.0421
MP4 energy (a.u.)	–	–	−1768.0143	−1768.0067	–	–
Adsorption energy (kcal/mol)	–	–	−16.28	−18.73	–	–

Table 2
Atomic properties resulting from calculations using catalyst model 2

	Model 2	NO	I-a	I-b	II-a	II-b
Bond length (Å)						
Cu–O	–	–	–	2.378	–	2.978
Cu–N	–	–	2.191	–	2.469	–
N–O	–	1.126	1.119	1.128	–	–
Atomic charge						
Cu	0.9207	–	0.8890	0.9020	0.9033	0.8888
Al	2.1491	2.1521	2.1504	2.1508	2.1492	
N	–	0.0952	0.0634	0.1602	0.0096	–
O of NO	–	−0.0952	−0.0473	−0.1494	–	0.0268
Atomic spin density						
Cu	0.0000	–	−0.0055	−0.0019	0.0107	−0.0056
Al	0.0000	–	0.0001	0.0001	0.0007	0.0000
N	–	0.8470	0.8417	0.8783	2.9883	–
O of NO	–	0.1530	0.1636	0.1236	–	2.0018
HF energy (a.u.)	−2182.2317	−129.2421	−2311.4828	−2311.4810	−2236.6168	−2257.0264
MP4 energy (a.u.)	–	–	−2312.1710	−2312.1672	–	–
Adsorption energy (kcal/mol)	–	–	−11.28	−9.07	–	–

Table 3
Frequency of NO comparing the observed value with the calculated value

Species	Observed value (cm^{-1})	Calculated value (cm^{-1})	
		Raw value	Scaled value[a]
Free NO	1904	2211	1904
NO on Cu^+ of Cu-ZSM-5	1807–1815	–	–
NO of I-a on model 2	–	2231	1921
NO of I-b on model 2	–	2192	1888

[a] The scale factor was adjusted at the frequency of free NO.

1 produces N_2 and O_2 smoothly and the reaction of route 2 produces O_2 with more difficulty. This result supports the experimental view that oxygen prevents the NO decomposition reaction on Cu-ZSM-5.

3. Conclusions

The calculations on the monodentate system, which consists of the combination of the two models and the two reaction routes shown in Figs. 1 and 2, suggests that NO decomposition on Cu-ZSM-5 can progress equally via both reaction routes. Although several experimental results such as the deactivation by oxygen can be explained and the profile of Cu-ZSM-5 catalyst can be represented by our calculation results, the IR spectrum shift of NO has not be reproduced. More accurate calculations or investigations on the bidentate system may be necessary to solve the remaining problems.

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References

[1] S. Huzinaga, Gaussian Basis Sets for Molecular Calculations, Elsevier Amsterdam (1984).
[2] M. Frisch, J. Foresman and A. Frisch, GAUSSIAN92, Gaussian Inc., Pittsburgh, PA (1992).
[3] J. Valyon and W.K. Hall, J. Phys. Chem., 97 (1993) 1204–1212.