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Fundamental study on the NO_x direct decomposition catalysts

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Abstract

We are developing direct decomposition catalysts to decompose the NO_x involved in high temperature exhaust gases to N_2 and O_2 without any reductants such as urea and plan to bring this technology into practice in the 21st century. We expect to create very simple deNO_x systems using direct decomposition catalysts applicable to a wide range of fields (co-generation, boilers, automobiles and so on) after overcoming the technical difficulties. Perovskite catalyst and zeolite catalyst are the most promising materials for direct decomposition catalysts. This study focuses on seeking and designing novel NO_x direct decomposition catalysts having high activities through theoretical studies using computational chemistry and experimental studies using surface-science techniques.

Keywords: NO_x reduction; Decomposition catalysts

1. Results and discussion

1.1. Theoretical study on perovskite catalysts

Perovskite catalysts showed little activity for NO decomposition at high temperature above 1000 K. In this study, we have been trying to design and develop perovskite catalysts with high activity for NO decomposition by using the molecular orbital theory.

Adsorption of NO at an oxygen vacancy of perovskite is thought to be the primary reaction of NO decomposition [1], Recently, Yasuda et al. showed in full detail that the rate-determining step for the direct decomposition of NO over $LaCuO_4$-based mixed oxide catalysts with perovskite-related structure is not the desorption of oxygen from the surface [2]. From this view point, one may say that NO adsorption and dissociation are essential for NO decomposition. Therefore, in order to investigate the mechanism of NO adsorption and dissociation, we have carried out molecular orbital calculations of cluster models for NO adsorption at the oxygen vacancy on the $LaCoO_3$ (001) surface, using the DV-Xα-cluster method, which has been proved to be very efficient in solving the

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Hartree–Fock–Slater equation for large clusters of metallic oxides [3].

First of all, the structure of the cluster is based on the model of the adsorbed structure which is proposed by Voorhoeve [4]. As shown in Fig. 1, C_{2v} symmetry is assumed on the cluster model (where V represents the oxygen vacancy). In the calculations, the distances V–O(NO) varied from 0 to 1 Å.

From the overlap population analysis, total N–O bond orders decrease as the NO molecule approaches the oxygen vacancy. The π-type bond orders depend largely on the V–O(NO) distance, due to the small difference in energy levels between the catalyst's Co 3d and NO's $2\pi^*$, because there is considerable interaction between them. However, the σ-type bond orders do not vary during the adsorption of NO to the oxygen vacancy, since the energy level of 5σ of NO is not close to that of the catalyst's Co3d, and almost no interaction occurs between them. Generally, a NO molecule has two π-type anti-bonding molecular orbitals ($2\pi_x^*$, $2\pi_y^*$), which can accommodate four electrons in total. In a neutral NO molecule, a molecular orbital in a $2\pi^*$ band which contains these two molecular orbitals is occupied by only one electron. When V–O(NO) distances are zero, the calculated overlap populations of individual π-type molecular orbitals are as indicated in Fig. 2, which shows the band structure of 1π (right: bonding area) and $2\pi^*$ (left: anti-bonding area)

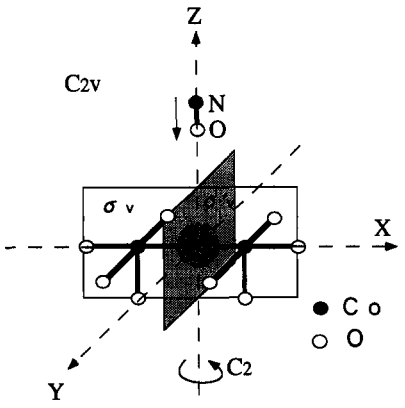

Fig. 1. Cluster model for NO adsorbing to oxygen vacancy.

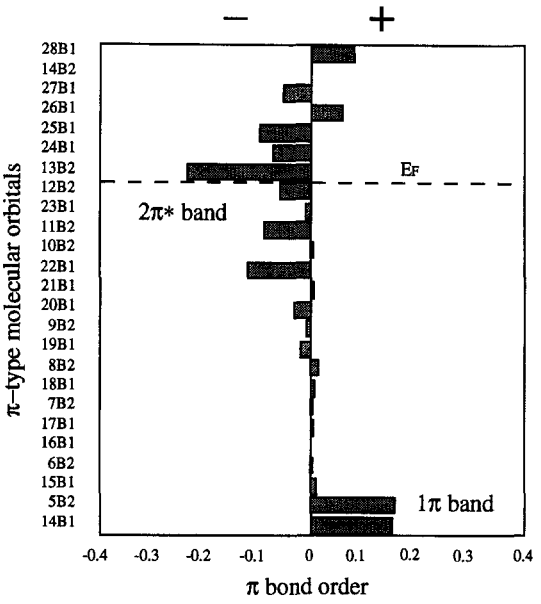

Fig. 2. Calculated overlap population of N–O bond.

of adsorbed NO. (EF represents Fermi level). Fig. 2 shows that almost half of the $2\pi^*$ band of adsorbed NO is occupied by electrons. Some of these electrons have moved form the catalyst, showing that back donation occurs from the catalyst's Co3d to the $2\pi^*$ of adsorbed NO. As a result, it appears that the N–O bond of the adsorbed NO at the oxygen vacancy weakens and dissociates at the primary step of NO decomposition.

1.2. Theoretical study on zeolite catalysts

The investigation consists of two parts. One concerns the reaction mechanism, the calculations on the reaction center being based on the molecular orbital method. The other concerns the structure of catalysts, the calculations on the bulk model of catalysts being based on the molecular orbital method together with molecular dynamics method under periodic boundary conditions. Our previous study, based on Hartree–Fock level calculations, cannot reproduce the frequency of NO adsorbed on Cu-ZSM-5 completely, because the electron correlation was disregarded [5].

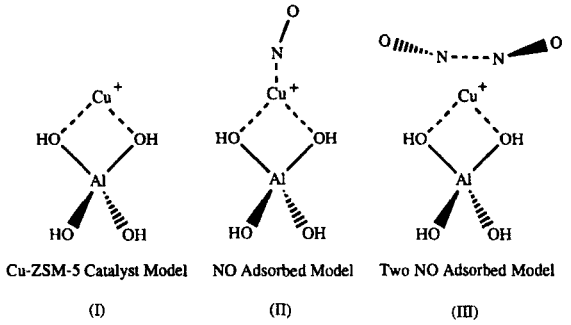

Fig. 3. Models used in the reaction center calculation.

On the investigation of the reaction mechanism, all calculations were performed using the BP86 method [6] as a density functional method while taking the electron correlation with Huzinaga's MIDI-P basis set [7] into consideration on several models, shown in Fig. 3, and $Cu^{+}[Al(OH)_4]^{-}$ (I) was used as the reaction center model. Calculation results on this model reproduce the frequency of adsorbed NO on Cu-ZSM-5 within an error of ±5% (Table 1) [8] and indicate that the adsorbance energy of (II) for NO is −51.0 kcal/mol and the stabilization energy from (II) to (III) is −18.5 kcal/mol.

Table 1
The frequency of adsorbed NO on Cu-ZSM-5 [6]

	Free NO	Adsorbed NO (II)	Adsorbed NO (III)
Calculated frequency (cm^{-1})	1875	1815	1748 (asym) 1642 (sym)
Observed frequency (cm^{-1})	1875.9	1807–1815	1825 (asym) 1732 (sym)

This suggests that all of the Cu sites in Cu-ZSM-5 are covered by one molecule of NO at first and then the remaining free NO can be adsorbed as a secondary NO. Fig. 4 shows the schematic route of two NO decompositions via N_2O yielding atomic oxygen. Since the enthalpy of the decomposition of adsorbed 2NO is very large, this reaction cannot progress spontaneously without the participation of the other molecules or formation energy such as the oxygen molecule (the calculated value is −139.8 kcal/mol for O_2 formation from 2O). After all, although the results of calculations on (II) and

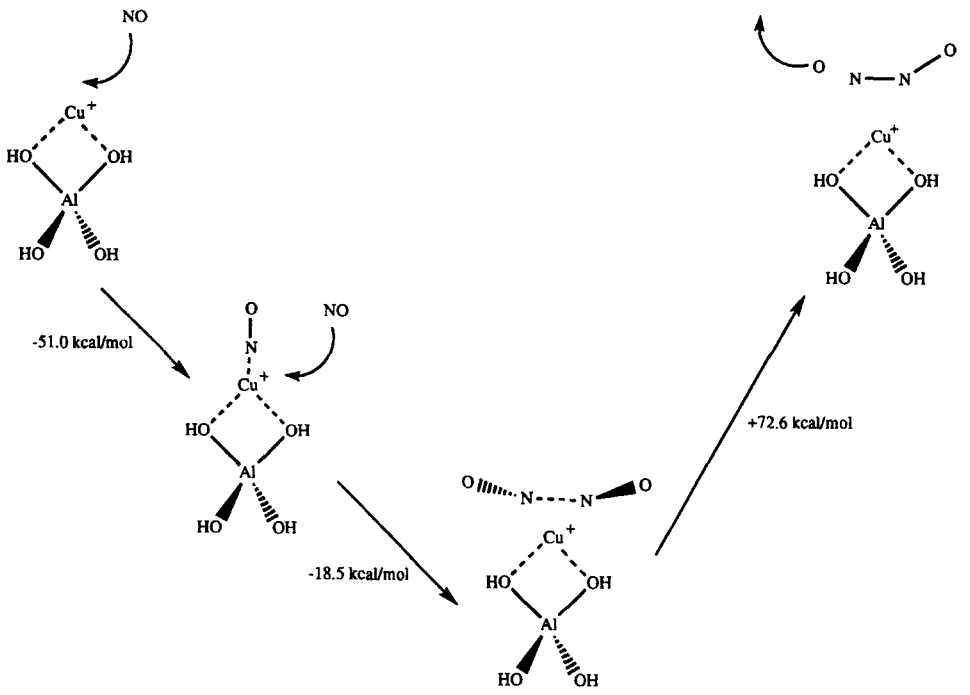

Fig. 4. Schematic route of twin NO decomposition via N_2O.

(III) show good accuracy, the dissociation energy of twin NO cannot be reproduced.

On the investigation of the structure of catalysts, Cerius2 [9] and MOPAC93 [10] were used to examine the stable structure of aluminosilicate ZSM-5, which contains an amount of aluminum atoms per unit cell at the same ratio as used in the experimental study (SiO_2/Al_2O_3 = 50). ZSM-5 has 8 equivalent atoms for each site (T1–T12). The calculations are carried out with the distinction of all equivalent atoms (96 position) and the positions of aluminum are decided stepwise from one aluminum substituted ZSM-5 to four aluminum substituted ZSM-5 using Na^+ as a charge compensating atom. The results of the calculations indicate that all aluminum atoms are situated at the T1 position (Fig. 5). However, there is an energy difference of about 10 kcal/mol between some stable structures. Therefore, substitutions to other positions can occur.

1.3. Surface science studies on model catalysts

The objectives of this study are: to synthesize novel model catalysts for NO_x direct decomposition by means of the latest preparation techniques possible to control the surface structure of the catalysts and to get an insight to develop a practical catalyst for NO_x direct decomposition through studying the structure and reaction mechanism of the model catalysts.

We noted copper as active site because copper catalysts such as Cu-ZSM-5 show the high-

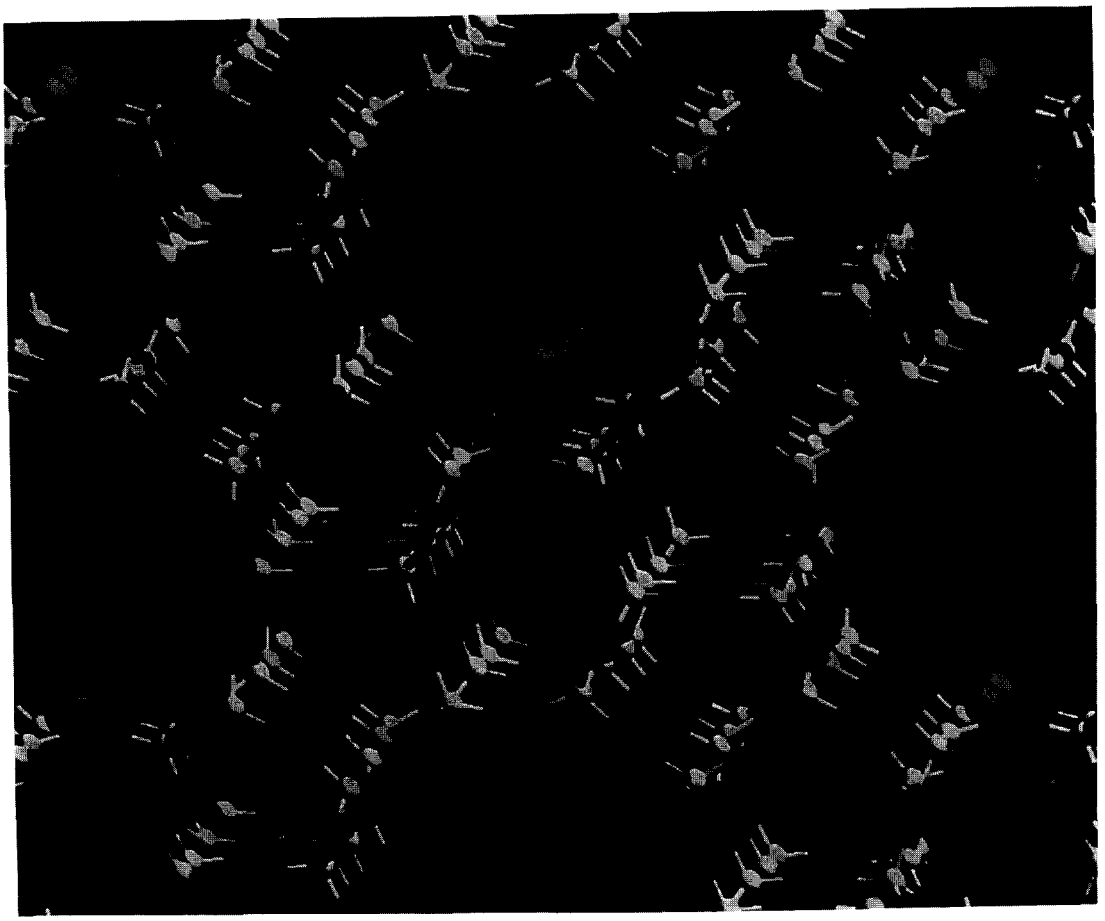

Fig. 5. Optimized structure of Cu-ZSM-5 (4 Al/cell).

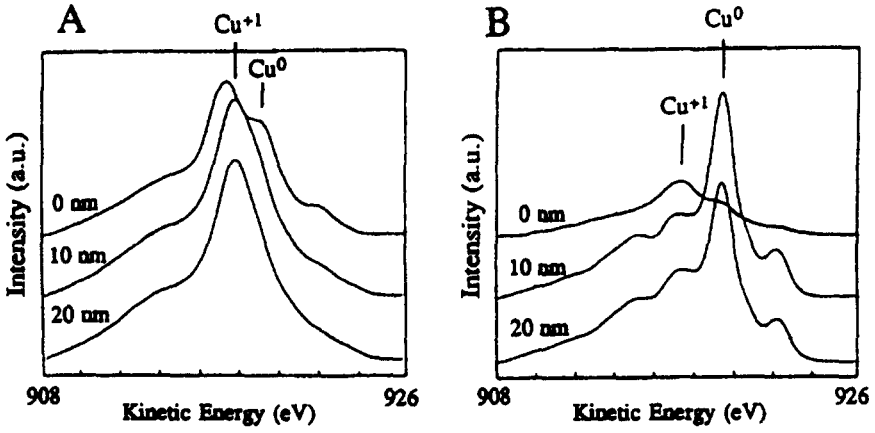

Fig. 6. Cu LMM spectra for copper oxide films before (A) and after (B) ion implantation.

est activity for NO_x decomposition. It is reported that Cu^+ acts as active site in catalytic reaction on Cu-ZSM-5 catalyst [11]. A possibility to develop activity by controlling the structure and the valence of copper is expected.

The model catalysts were synthesized by Si ion implantation into copper oxide thin films, e.g., copper atoms on aluminosilicate, that is, Cu-ZSM-5. The copper oxide films were prepared with laser ablation. The conditions of laser ablation and ion implantation are shown in Table 2.

The model catalyst was evaluated by X-ray photoelectron spectroscopy (XPS). Figs. 6 and 7 show Cu LMM Auger electron and O 1s photoelectron spectra, respectively, for copper oxide films before and after ion implantation. The copper oxide films were sputtered by 0.6 keV Ar ions with no cooling during depth profiling. Spectra of the top surface were affected by oxidation by air, since preparation and evaluation of the model catalyst were performed with separate instruments. In Cu LMM Auger spectra, Cu^+ is the main component before ion implantation. On the other hand, the Cu^0 peak intensity is increased after ion implantation. Furthermore, O 1s spectra show formation of a Si–O bond by Si ion implantation. These results suggest that implanted ions bond to oxygen atoms, so that the valence of the copper atom is reduced. It is confirmed that the valence of the copper atom can be controlled by ion implanta-

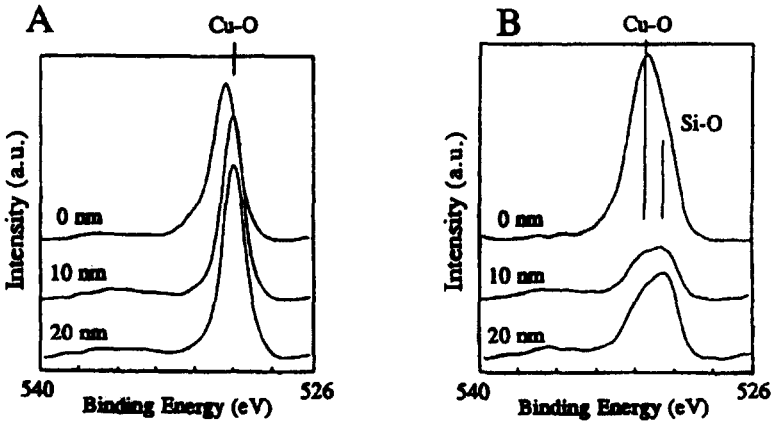

Fig. 7. O 1s spectra for copper oxide films before (A) and after (B) ion implantation.

Table 2
Conditions of preparation of model catalyst

Laser ablation	
Substrate	Polycrystalline tantalum sheet (99.95%)
Target	Pellet prepared by pressing and calcining of CuO powder (99.99%)
Laser	248 nm, 500–670 mJ/shot[28]
Ion implantation	
Ion species	Si^+, 30 keV
Angle	7 degrees
Amount of ion dose	$2\times10^{16}/cm^2$

tion, though XPS depth profile might be observed at a more reduced state than the real state because of selective sputtering.

The evaluation of the catalytic activity of a model catalyst by ultra high vacuum temperature programmed desorption (UHV-TPD) and the preparation of new model catalysts by another method are designed.

Acknowledgements

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