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Theoretical study of NO adsorbed on the surface of TiO_2(110) cluster model

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Abstract: The chemisorption properties of $N^{18}O$ adsorption on TiO_2(110) surface were investigated by experimental and theoretical methods. The results of temperature programmed desorption (TPD) indicated that the temperatures of the three desorption peaks of the main N_2 molecules were at (low) temperature of 230 K, 450 K, and (high) temperature of 980 K. This meant that $N^{18}O$ decomposed and recombined during the process of N_2 desorption after $N^{18}O$ was exposed. Analysis of the stable combination and orbital theory calculation of the surface reaction of NO adsorption on the TiO_2(110) cluster model showed that there was clear preference for the Ti-NO orientation.

Key words: Adsorption, TPD, Cluster model, Molecular orbital theory calculation
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INTRODUCTION

The adsorption of gas molecules on metals, metal oxides or alloys had been researched widely to find a solution for the problem of air pollution (Davies and Craig Jr., 2003; Yanagisawa, 1996; Tominaga *et al.*, 1999). NO could be adsorbed on the particle surface and desorbed as N_2 from the surface by temperature programmed desorption (TPD) (Davies and Craig Jr., 2003; Yanagisawa, 1996). The calculation of cluster model was established with molecular orbital (MO) theory (Ryu *et al.*, 1999; Shimizu and Tachikawa, 2002). We are interested in studying the mechanism of the adsorption and desorption of NO on the surface of TiO_2 (110); and try to establish a cluster model for calculating the NO absorption on the TiO_2 with both MOPAC and GAUSSIAN and determining the chemisorption properties of the surface reaction.

EXPERIMENTAL AND COMPUTATIONAL METHODS

TiO_2 powder was preheated at 1123 K for two hours and then allowed to return to room temperature; after which its surface was cleaned by TPD in ultra-high vacuum system. TPD measurements were carried out from low temperature to high temperature. The purity of ^{18}O and ^{15}N of the $N^{18}O$ absorption gas were respectively measured as 97.5% and 99.8% with base pressure of 10^{-5} Pa by quadrupole mass spectroscopy (QMS). In order to confirm the cleanness of the TiO_2 surface after annealing, the elements of the surface were measured using Auger electron spectroscopy (AES).

The (110) surface of TiO_2 has been investigated extensively as this surface is thermodynamically the most stable (Linsebigler *et al.*, 1995). Upon heating at high temperatures other surface orientations would reconstruct leading to (110) facets (Sorescu and Yates Jr., 2002). It is proper to adopt the (110) cluster model in MO calculation. Ti_5O_{10} is a representation of the cluster model for describing the TiO_2 (110) surface. Semi-empirical molecular orbital theory (MOPAC 93) was used to calculate the Ti_5O_{10} cluster, and Schierbaum's GAUSSIAN (semi-empirical molecular orbital method) was used to calculate the energy level of the NO adsorption on the Ti_5O_{10} cluster.

RESULTS AND DISCUSSION

Temperature-programmed desorption results

The TPD profiles of the main N_2 gas were observed after 1000 L of the $N^{18}O$ gas was exposed to temperature of 150 K at heating rate of 0.8 K/s and 1300 L of the $N^{18}O$ gas was exposed to room temperature at heating rate of 0.5 K/s (Fig.1). The peak (I, II, III) temperatures of N_2 desorption were 230 K, 450 K and 980 K, respectively. Their activation energies were 0.23 eV, 0.68 eV and 2.5 eV from low temperature to high temperature. It was suggested that there was a vacancy of Os on the preheated surface (Gopel and Rocker, 1983), and that the $N^{18}O$ could be adsorbed on the Os vacancies, where the $N^{18}O$ was decomposed and N-N recombined as N_2 desorption. Therefore, in the whole process, two chemical reactions occurred on the TiO_2 surface after the $N^{18}O$ was exposed. At high temperature the activation was energy is enough to produce new vacancies and support chemical reaction on the surface, so the intensity of N_2 desorption increased at high temperature.

Results of NO adsorption on the TiO_2(110) cluster

Molecular orbital (MO) calculation results were used to describe the stable combine of the NO adsorbed on the TiO_2(110) cluster and to investigate the chemisorption properties of the surface reaction.

(1) MOPAC (Semi-empirical molecular orbital calculation)

The Ti_5O_{10} model was based on the TiO_2(110) cluster, where Ti and O of the Ti_5O_{10} were regarded as (+4) and (–2) charges respectively. The result of MOPAC calculation showed that the band gap of the Ti_5O_{10} was 4.00 eV, whose previous value was 3.10 eV. The charges distribution is shown in Fig.2.

The band gaps of the NO molecule on the Ti_5O_{10} cluster with the two orientations were calculated. We analyzed both orientations of the NO

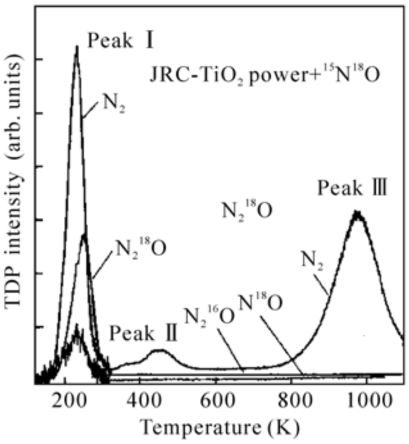

Fig.1 Desorption spectrum of the NO adsorbed on the TiO_2 powder surface

The desorption of gases N_2, $N_2{}^{18}O$ and $N^{18}O$ occurred at 150 K–300 K, and the desorption of gases N_2, $N_2{}^{16}O$ and $N^{18}O$ at 300 K–1050 K

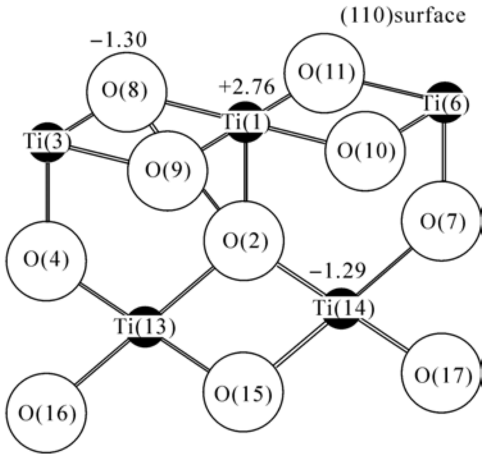

Fig.2 Ti_5O_{10} model from TiO_2 (110) cluster

The distribution of charges Ti(1), O(2) and O(8) are +2.76, –1.29, –1.30, respectively molecule with either end toward the surface. The Fig.3 of the Ti-NO bond of the cluster shows that the Ti charge (1) is +2.81, and O(2), O(8), O(9), O(10), O(11) are all −1.36 respectively. The NO charge is –0.87. The absorption energy (stable energy) for Ti-NO is 1.66 eV. Compared with the energy gap of 2.11 eV for the HOMO-LUMO energy of Ti-NO, the absorption energy was small. Consequently, its Ti-NO geometry is stable. Fig.4 of the Ti-ON bond of the cluster shows that the charge distribution value of Ti(1) is +2.82, and that of O(2), O(8), O(9), O(10), O(11) are all −1.38, respectively. The NO charge is −0.75. In this case the energy gap of 2.66 eV for Ti-ON is bigger than that of 2.11 eV for Ti-NO, so the Ti-NO geometry causes Ti-NO to be easily combined.

The results indicated that the most stable configuration was a tilted geometry of the NO molecule with N atom toward the surface. This is clear preference for the Ti-NO orientation compared to the Ti-ON configuration (Sorescu *et al.*, 2000).

At high temperature there are more molecules of Ti-NO bonds of the clusters to get the enough activation energy of 2.5 eV in the experiment to achieve the transition over the gap energy of 2.11 eV, then the NO is decomposed and N-N recombined as N_2 desorption. The intensity of N_2 desorption increases by the Ti-NO bond accorded well with the experimental results at high temperature.

Previous experimental studies (Boccuzzi *et al.*, 1991) revealed that on the annealed, defective TiO_2 surface, N_2O was formed by a reduction process. The result obtained on the oxidized surface indicated that adsorption of N_2O could occur through a vertical configuration in which the Ti-N-N-O orientation was slightly more stable than the Ti-O-N-N geometry. The adsorption energies for these two configurations were small. Consequently, such species can be found on the surface only at low temperatures (Sorescu and Yates, 2002). N_2O desorption being observed only at low temperatures (Fig.1) accorded even better with experimental results.

(2) GAUSSIAN (semi-empirical molecular orbital calculation)

Ti-NO bond of the Ti_5O_{10} cluster was also calculated by GAUSSIAN (Fig.5). Table 1 shows the change of the charges distribution for the NO adsorption on the Ti_5O_{10} cluster calculated by GAUSSIAN and MOPAC method. The change of charge distribution of the NO by GAUSSIAN is smaller than that of NO by MOPAC. To gain the exactitude of change of the charges distribution by GAUSSIAN, the atom amount of the TiO_2 (110) cluster must be increased to calculate.

Since the stable energy (0.45 eV) of the NO adsorbed on the Ti_5O_{10} cluster is very small by GAUSSIAN, the process can be regarded as physical absorption. The energy level of the NO adsorption on the Ti_5O_{10} cluster is shown in Fig.6.

The energy of LUMO and HOMO of the Ti_5O_{10} is higher than that of the NO, respectively. If the or-

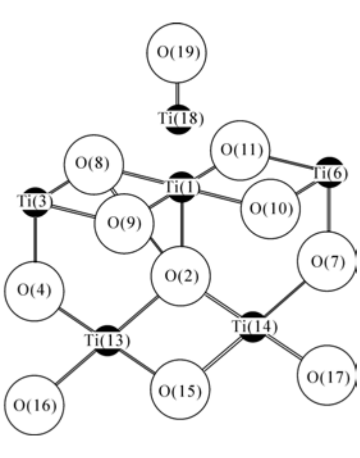

Fig.3 Ti-NO bond of the Ti_5O_{10} cluster
The distance of Ti (1)-N (18) is 1.85 Å, and N(18)-O(19) is 1.20 Å

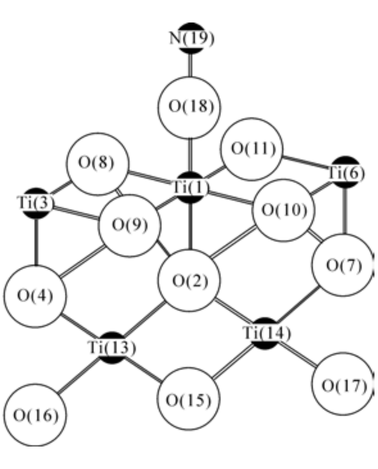

Fig.4 Ti-ON bond of the Ti_5O_{10} cluster
The distance of Ti (1)-O (18) is 1.55 Å, and N (19)-O (18) is 1.20 Å

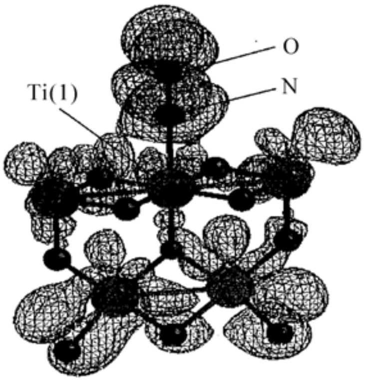

Fig.5 Ti-NO bond of the Ti_5O_{10} cluster
The big ball is for Ti, the small ball is for O, and the net is for the top charges of Ti, O and N

Table 1 The change of charges distribution of the NO adsorption on the Ti_5O_{10} cluster

Cluster	Charge	GAUSSIAN Calculation	MOPAC Calculation
Ti_5O_{10}	Ti (1)	+0.85	+2.76
NO	NO	0	0
Ti_5O_{10}/NO	Ti (1)	+1.22	+2.81
(Ti-NO)	NO	+0.09	–0.87

bital symmetry is ignored, the electrons of HOMO energy of the NO could transfer to LUMO energy of the Ti_5O_{10}. The NO absorption on the TiO_2(110) for Ti-NO geometry is combined stably.

CONCLUSION

The results of the $N^{18}O$ adsorption on the TiO_2 surface by TPD indicated that the temperatures of the three desorption peaks of the main N_2 molecules are 230 K, 450 K and high temperature 980 K. The peak of N_2O desorption is observed only at low temperatures.

There is a clear preference for the Ti-NO orientation compared to the Ti-ON by MOPAC calculation of the NO molecule on the Ti_5O_{10} cluster. The NO absorption on the TiO_2(110) for Ti-NO geometry is combined stably by GAUSSIAN calculation and is in good agreement with the MOPAC calculation results.

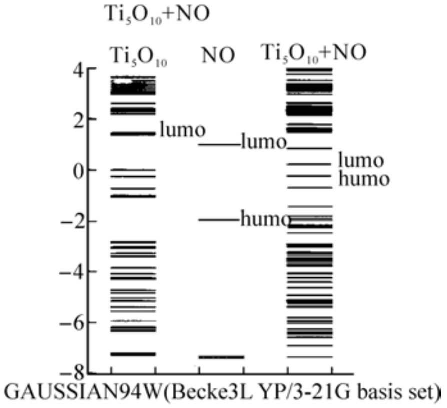

Fig.6 The energy lever of the NO adsorption on the Ti_5O_{10} cluster

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