

Conversion of N₂O to N₂ on MgO (001) Surface with Vacancy: A DFT Study

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The adsorption and decomposition of N₂O at regular and defect sites of MgO (001) surface have been studied using cluster models embedded in a large array of point charges (PCs) by DFT/B3LYP method. The results indicate that the MgO (001) surface with oxygen vacancies exhibits high catalytic reactivity toward N₂O adsorptive-decomposition. It is different from the regular MgO surface or the surface with magnesium vacancies. Much elongation of O—N bond of N₂O after adsorption at oxygen vacancy site with O end down shows that O—N bond has been broken with concurrent production of N₂, leaving a regular site instead of the original oxygen vacancy site (F center). The MgO (001) surface with magnesium vacancies hardly exhibits catalytic reactivity. It can be concluded that N₂O dissociation likely occurs at oxygen vacancy sites of MgO (001) surface, which is consistent with the generally accepted viewpoint in the experiments. The potential energy surface (PES) reflects that the dissociation process of N₂O does not virtually need to surmount a given energy barrier.

Keywords N₂O, N₂, MgO (001) surface, density functional theory

Introduction

The destruction or removal of nitrogen oxides (DeNO_x process) is a very important issue in our industrial society and environmental catalysis due to their negative effects in environmental pollution and chemical processing.¹⁻⁸ Thus, stringent federal and environmental regulations have placed a high priority on developing catalysts to prevent these pollutants from entering the earth's atmosphere. Metal oxides, as a general class of materials, have shown great promise in such applications.^{9,10} In fact, the surface chemistry of oxides is relevant to many technological applications: catalysis, photo-electrolysis, electron-device fabrication, corrosion prevention, sensor development, etc.¹¹ Accordingly, there have been a lot of experimental and theoretical studies on the interaction of nitrogen oxides (NO, NO₂ and N₂O) with the surface of metal oxides.¹²⁻¹⁷

N₂O is a pollutant produced as a byproduct from several industrial processes. From the viewpoint of environment, it contributes to stratospheric ozone layer depletion and is thought to be responsible for "Global Warming".¹⁸⁻²⁰ So, the catalytic removal of N₂O is vital to environmental protection. Various types of catalysts have been reported for the decomposition of nitrous oxides.²¹ However, here, we will focus only on metal oxides. Alkaline earth metal oxides (MgO, CaO and BaO) have been widely investigated as a catalyst system.^{15,22-25} The details regarding the progress of N₂O on metal oxides in experimental and theoretical study have been comprehensively introduced in the papers of Lu *et al.*¹⁵ and Snis *et al.*²² Very recently, Nakamura *et al.* and Pettersson *et al.* studied the decomposition of N₂O to N₂.^{24,25} They both proposed that surface peroxide ions (O₂²⁻) of the substrate are involved in the mechanism of N₂O decomposition reaction. Their studies indicate that the reactivity toward N₂O decomposition is in the sequence of MgO, CaO, SrO, and BaO. However, it can be seen that these studies are mainly focused on the decomposition of N₂O at terrace oxygen sites of the metal oxides surface. What specific role of the different vacancies of MgO (001) surface, such as magnesium and oxygen vacancies, involved in the activation of N₂O remains unclear.

So far, systematic theoretical work regarding N₂O adsorption on MgO is scarce. Some relevant works are *ab initio* calculations of N₂O adsorption at CaO surface.^{26,27} As is known, in a kinetic process, the adsorption is an important stage for the decomposition of gas molecules. Thus, the understanding of N₂O adsorption at MgO (001) surface from the molecular level should be necessary and interesting, especially for the MgO (001) surface with vacancies due to its higher catalytic reactivity. The aim of the present paper is to investigate the N₂O adsorption at perfect and defect sites (edge, corner, oxygen vacancy and magnesium vacancy sites) of MgO (001) surface.

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Calculation model and details

Solid MgO has the rock-salt structure with its nearest Mg—O distance being 0.2104 nm.²⁸ In this work , small stoichiometric MgO clusters with various size are used : O_9Mg_9 represents a five-coordinated O^{2-} adsorption site at a perfect surface (O_{5c}), O_6Mg_6 , a four-coordinated O^{2-} adsorption site at the edge (O_{4c}), and O_4Mg_4 , a three-coordinated O^{2-} adsorption site at the corner (O_{3c}). Similarly, the Mg_9O_9 , Mg_6O_6 , and Mg_4O_4 cluster models represent the regular (Mg_{5c}), edge (Mg_{4c}) and corner (Mg_{3c}) Mg^{2+} adsorption sites, respectively. This cluster model approach has been widely used to study the adsorption and reaction of molecules with oxide surfaces and it properly describes the physics of local surface processes.²⁹⁻³² At the same time, our models conform to the three principles for the cluster modeling of metal oxides suggested by Lu *et al.*, *i. e.*, the neutrality principle, the stoichiometry principle and the coordination principle.³³ Similar cluster models have been employed to investigate CO adsorption on the MgO (001) surface in our previous study,³⁶ where the calculated results in qualitative agreement with experiments were obtained. $Mg_{13}O_{12}$ and $O_{13}Mg_{12}$ are used to represent the defect sites of MgO (001) surface with neutral oxygen vacancy and magnesium vacancy. Pacchioni *et al.* have successfully studied metal atom adsorption at the magnesium and oxygen vacancy sites and CO adsorption at oxygen vacancy site of MgO (001) surface, respectively, by similar cluster models.^{34, 35} Different sizes of cluster models, Mg_5O_5 , Mg_9O_9 and $Mg_{13}O_{13}$, are employed to study N_2O adsorption at the regular site of MgO (001) surface. Their results show that the optimized geometries and adsorption energies are almost independent of cluster size, which is also found in the calculation of CO adsorption on MgO (001) surface.³⁶ So, we believe that our cluster models can give the results at a good confidence level.

All these cluster models are embedded in a large array of ± 2.0 point charges (PCs) to take into account the stabilizing effect of the rest of the crystal and in particular to ensure that the Madelung potential in the chemisorption region is properly described.³⁷ To circumvent unphysical electron transfer from the quantum cluster to positive embedding point charges, the nearest positive PCs at the boundary are further augmented with Ne-core potentials of Mg.³⁸

The adsorption energies are defined positive for a stable adsorbate/substrate system : $E_{ads} = E_{N_2O} + E_{MgO} - E_{(MgO+N_2O)}$, where $E_{(MgO+N_2O)}$ is the energy of adsorbate/substrate system in the equilibrium state, E_{N_2O} and E_{MgO} those of the adsorbate and substrate alone, respectively. We have applied the standard counterpoise method³⁹ to account for the basis set superposition errors (BSSE) for the calculations of adsorption energies, even though our main interest here is in qualitative trends in the energetics, not in absolute values.

For all the calculations throughout, we used the hy-

brid density functional B3LYP^{40, 41} method in the Gaussian-98 program.⁴² The DFT/B3LYP method includes a three-parameter hybrid density functional that combines the gradient-corrected exchange functional of Becke and the correlation-functional of Lee, Yang, and Parr with Hartree-Fock exchange. It is generally agreed that DFT methods give quite accurate results for solid systems.⁴³ Especially with the B3LYP method, many reasonable predictions of the adsorbate structure and adsorption energies have been made. The basis sets used herein are the standard 6-31G (d) for N, O and Mg. For the free N_2O molecule, the calculated N—N and N—O bond length are 0.1134 nm and 0.1192 nm, in good agreement with the experimental values of 0.1126 nm and 0.1188 nm, respectively.⁴⁴ Good calculated results in line with experimental data were successfully obtained in previous study regarding CO and NO adsorption on MgO (001) surface with this basis sets by DFT/B3LYP method.^{45, 46} The adsorption geometries of N_2O were optimized in internal coordinates with all the substrate atoms being fixed at the bulk values. Optimizations have been done by using the Berny algorithm with the Gaussian-98 program.⁴²

Results and discussion

N_2O adsorption at regular, edge and corner site of MgO (001) surface

Table 1 gives the calculated results for N_2O adsorption at regular, edge and corner site of MgO (001) surface. It can be obviously seen that the adsorption energy is larger for N_2O at Mg^{2+} site than that at O^{2-} site, indicating that N_2O prefers to adsorb at Mg^{2+} site. In addition, it is more advantageous for N_2O with N towards the surface cationic site. Especially for N_2O adsorbed at corner cationic site of MgO (001) surface, it has the large adsorption energy 0.52 eV and 0.61 eV, corresponding to the adsorption modes of N_2O via O atom and N atom bound to the surface, respectively. It can be predicted that strong bond is formed between N_2O molecule and the MgO (001) surface. As regards other adsorption models, it can be concluded that the interaction between the N_2O and MgO (001) surface are primarily electrostatic interaction due to their rather small adsorption energies (< 0.3 eV, see Table 1). Note that the adsorption (with negative adsorption energies) is not stable for N_2O adsorbed at edge and corner cationic site with the axis of molecule parallel to the MgO (001) surface. Even if N_2O is flat adsorbed at regular Mg^{2+} site, the adsorption energy (0.08 eV) is rather small. These indicate that this kind of adsorption mode is relatively disadvantageous with respect to other two adsorption ones. On the other hand, for N_2O adsorbed at O^{2-} site of MgO (001) surface, it prefers to adsorb flat at the O^{2-} site of MgO (001) surface. In short, energetically, the corner Mg^{2+} site is the most favorable position for N_2O . However, it should be noted that the adsorption

strength is weak and the N—N and N—O bonds are hardly perturbed for N_2O adsorption at regular, edge or corner site of $MgO(001)$ surface, compared to the free N_2O molecule. Obviously, this is not conducive to the dissocia-

tion of N_2O . So, the regular, edge and corner Mg^{2+} or O^{2-} sites of $MgO(001)$ surface hardly exhibit the catalytic reactivity toward N_2O decomposition.

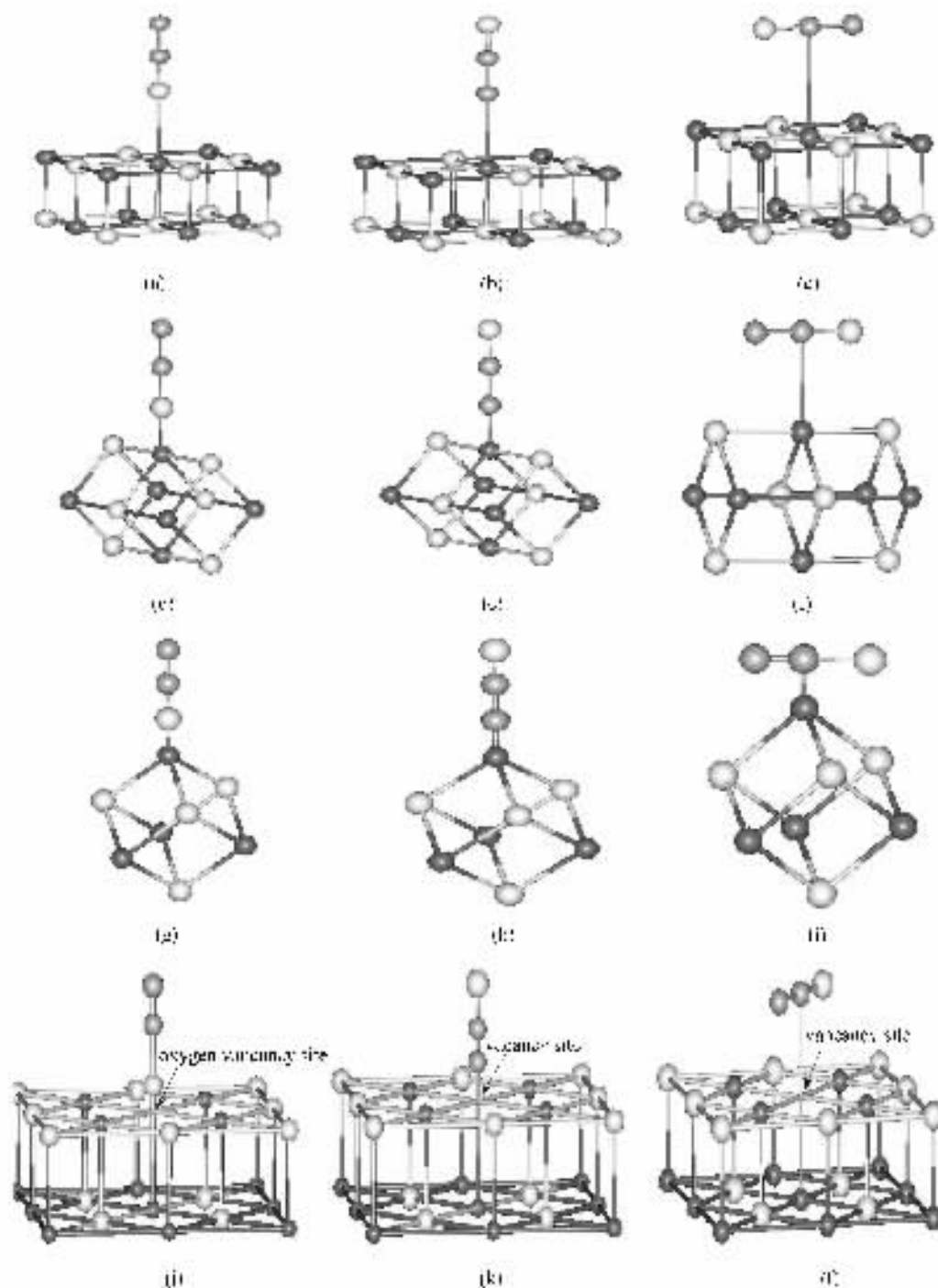


Fig. 1 Cluster models of N_2O adsorption at different sites of $MgO(001)$ surface : (a) (b) and (c) represent three different kinds of N_2O adsorption modes at regular cationic site (Mg_{5c}) of $MgO(001)$ surface ; (d) , (e) and (f) for adsorption at edge site (Mg_{4c}) ; (g) , (h) and (i) for adsorption at corner site (Mg_{3c}) ; (j) , (k) and (l) for adsorption at oxygen vacancy site (F center). The black spheres represent Mg atoms , the grayish ones N atoms , and the white ones O atoms respectively. Cluster models of N_2O adsorption at regular (O_{5c}) , edge (O_{4c}) and corner (O_{3c}) anionic site , and magnesium vacancy site of $MgO(001)$ surface are similar , not shown here. The embedded large array of point charges and Ne-core potentials of Mg are also not shown in the figure .

Table 1 Optimized geometries R ($\times 10^{-1}$ nm) and adsorption energies E_{ads} (eV) for N_2O adsorbed at regular , edge and corner Mg^{2+} sites and O^{2-} sites of MgO (001) surface

Cluster model	$R_{\text{x1-x2}}$	$R_{\text{O-N}}$	$R_{\text{N-N}}$	E_{ads}	E_{ads}^a
Mg _{5c} -ONN	2.557	1.201	1.129	0.19	0.34
Mg _{5c} -NNO	2.472	1.181	1.135	0.22	0.36
Mg _{5c} -flat NNO	3.458	1.194	1.135	0.08	0.24
Mg _{4c} -ONN	2.308	1.198	1.129	0.21	0.34
Mg _{4c} -NNO	2.321	1.181	1.134	0.25	0.42
Mg _{4c} -flat NNO	3.884	1.194	1.134	-0.03	0.12
Mg _{3c} -ONN	2.112	1.201	1.126	0.52	0.62
Mg _{3c} -NNO	2.200	1.184	1.134	0.61	0.71
Mg _{3c} -flat NNO	3.212	1.195	1.136	-0.05	0.07
O _{5c} -ONN	2.998	1.197	1.134	0.01	0.15
O _{5c} -NNO	2.349	1.193	1.135	-0.01	0.14
O _{5c} -flat NNO	2.901	1.194	1.133	0.14	0.30
O _{4c} -ONN	3.333	1.192	1.135	-0.03	0.10
O _{4c} -NNO	3.630	1.196	1.133	-0.04	0.10
O _{4c} -flat NNO	2.765	1.193	1.132	0.17	0.31
O _{3c} -ONN	3.358	1.190	1.137	-0.09	0.03
O _{3c} -NNO	3.837	1.198	1.134	-0.10	0.02
O _{3c} -flat NNO	2.817	1.192	1.132	0.08	0.21

^a Denotes the adsorption energy with BSSE correction.

Table 2 The optimized geometries R ($\times 10^{-1}$ nm) and adsorption energies E_{ads} (eV) for N_2O adsorbed at oxygen vacancy and magnesium vacancy sites of MgO (001) surface

Cluster model	$R_{\text{x1-x2}}$	$R_{\text{O-N}}$	$R_{\text{N-N}}$	E_{ads}	E_{ads}^a
O vacancy-ONN	0.038	2.921	1.106	6.29	6.50
O vacancy-NNO	1.854	1.155	1.151	1.56	1.75
O vacancy-flat NNO	0.632	1.192	1.136	1.69	1.84
Mg vacancy-ONN	0.647	1.216	1.130	-0.26	0.01
Mg vacancy-NNO	0.714	1.187	1.157	-0.38	-0.14
Mg vacancy-flat NNO	1.509	1.200	1.177	0.38	0.59
Free N_2O	—	1.192	1.134		
Free N_2	—	—	1.106		

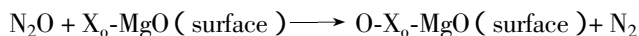
^a Denotes the adsorption energy without BSSE correction.

N_2O adsorption at vacancy site of MgO (001) surface

Both experiments and theoretical investigations have shown that MgO (001) surface with various vacancies has high catalytic reactivity toward gas molecules.⁴⁷⁻⁵⁰ For example, Pacchioni *et al.* used Hartee-Fock method to investigate the interaction of gas-phase CO and O_2 molecules with oxygen vacancy of MgO (001) surface.³⁵ It was found that the surface oxygen vacancies (F centers) exhibit a high reactivity toward CO and O_2 , which is different from the regular MgO (001) surface. The reaction proceeds through the formation of radical anions, CO^- and O_2^- , via the transfer of one electron trapped in the surface cavity to the empty levels of the adsorbed molecule. Table 2 lists the optimized geometries and adsorption energies for N_2O at oxygen and magnesium vacancy site of MgO (001) surface. We can find that both large adsorption energies and large elongation of the N—O bond of N_2O molecule are ob-

tained when N_2O approaches the oxygen vacancy site with O atom end down. This is particularly important in the case of N_2O , because in a kinetic process it will increase the residence time of the molecule on the surface and enhance the probability and rate for N_2O dissociation. In fact, the rather large bond length of N—O (0.2921 nm) and little Mulliken overlap-population (0.0020) of N—O of N_2O after adsorption indicate that N—O bond has been broken. Moreover, the N—N bond length of N_2O after adsorption is almost equal to that of free N_2 . All these propose that MgO (001) surface with oxygen vacancies contributes to the decomposition of N_2O with the concurrent production of N_2 , leaving an oxygen atom and forming a regular site instead of original F center. At the same time, it is noted that the O site of N_2O is almost completely inserted into the crystal lattice, leading to the high stabilization due to the Madelung potential. This can account for the large adsorption energy of N_2O adsorbed on MgO (001) surface with oxygen end toward the vacancy site (F

center). For the dissociative process of N_2O at oxygen vacancy site of $MgO(001)$ surface:



Here, X_o represents the oxygen vacancy site (F center) of $MgO(001)$ surface; the energy released in this reaction was calculated to be about 475 kJ/mol. Thus, the dissociation of N_2O is an energetically favorable process.

Regarding the adsorption modes, N_2O flat at F center or N end towards F center respectively, there are relatively large adsorption energies compared to those on the regular $MgO(001)$ surface. However, the geometries of N_2O are almost not perturbed, *i. e.*, the respective N—N and N—O bond length of N_2O is nearly unchanged. For the $MgO(001)$ surface with Mg vacancy, there is a small adsorption energy 0.38 eV concerning N_2O flat adsorption at Mg vacancy site of $MgO(001)$ surface. The interactions between N_2O and the $MgO(001)$ surface are repulsive for the other two adsorption modes, which can be reflected by their negative adsorption energies. Obviously, $MgO(001)$ surface with Mg vacancies exhibits almost no catalytic reactivity toward N_2O adsorptive-decomposition.

Based on the above discussions, one possible dissociation mechanism of N_2O on $MgO(001)$ surface is proposed, in which the surface oxygen vacancy sites of $MgO(001)$ surface are likely responsible for N_2O decomposition. This is consistent with the generally accepted standpoint.⁵¹⁻⁵³

Comparison of N_2O with NO adsorbed at oxygen vacancy site of $MgO(001)$ surface

More recently, Pacchioni *et al.* reported the conversion of NO to N_2O on $MgO(001)$ thin films by thermal desorption spectroscopy (TDS) and Fourier transform infrared (FTIR) spectroscopy and, on the other side, defining the geometries by *ab initio* DFT/B3LYP cluster model calculations.⁵⁴ They found that the conversion of NO to N_2O occurs preferentially at neutral oxygen vacancies (F centers). The N—O bond is broken much more when NO adsorbed at F center, especially with O end toward the vacancy site, with the bond length of NO changed from 0.116 nm of free NO to 0.149 nm. After another NO molecule approaches the adsorbed one, the original N—O bond in the adsorbed system O—N—N—O will be further weakened so as to decompose the N—O bond with concurrent N_2O , leaving the O in the lattice vacancy site of $MgO(001)$ surface. For comparison, we also calculate the adsorption of NO at neutral oxygen vacancy site. And, the geometry after another NO attaches the adsorbed one is also investigated. Our results are qualitatively consistent with those reported by Pacchioni *et al.* Namely, N_2O_2 can spontaneously dissociate into $O_{\text{lattice}} + N_2O$ at the terrace oxygen vacancy site (F center), with virtually no energy barrier, 0.1 eV. However, it is not clear how the N_2O changes at vacancy sites of $MgO(001)$ surface. In the

present paper, we put forward that the O—N bond of N_2O will be broken if N_2O molecule directly approaches F center, which can be demonstrated by the optimized geometric structures (see Table 2). Moreover, this process is largely exothermic with released reaction energy 475 kJ/mol. In order to deeply understand the dissociation process of N_2O at F center of $MgO(001)$ surface, we have calculated the potential energy surface (PES) of this system (see Fig. 2). Generally, it is not possible to calculate a realistic potential energy surface (PES) for even the simplest system. This is not surprising when one considers that even for the case of a simple diatomic molecule approaching a surface, the PES is in principle six dimensional and to map it fully is actually impossible. Most work therefore adopts some approximations and concentrates on a two-dimensional section of the PES. In the PES herein, the two variables, R_{X-O} and R_{O-N} , are considered, and the other degrees of freedom are fixed. The scan intervals of R_{X-O} and R_{O-N} are 0.004—0.224 nm and 0.119—0.320 nm, respectively. As can be seen from the PES, the dissociation process of N_2O does not virtually need to surmount an energy barrier, 0.13 eV. Namely, the conversion of N_2O to N_2 at F center of $MgO(001)$ surface is almost spontaneous, which is similar to the dissociation of N_2O_2 to N_2O . In fact, the higher catalytic reactivity of $MgO(001)$ surface with neutral oxygen vacancy (F center) is closely related to its unusual electronic structure, with free electrons in the cavity.^{35 55-58}

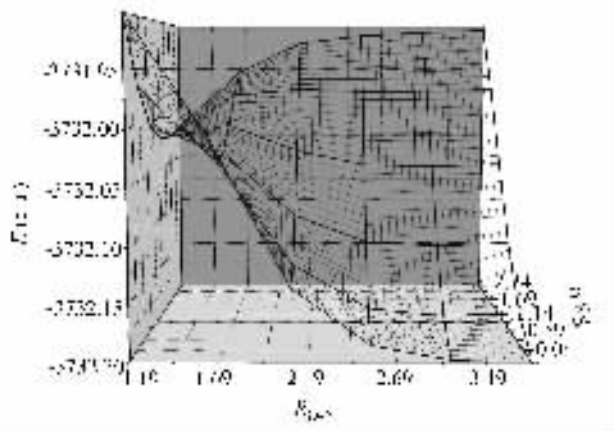


Fig. 2 Potential energy surface of N_2O adsorbed at oxygen vacancy site of $MgO(001)$ surface.

Conclusions

The results of N_2O adsorption and decomposition at regular and vacancy sites of $MgO(001)$ surface can be summarized as follows:

- (1) N_2O prefers to adsorb at regular, edge and corner Mg^{2+} site with N end down on $MgO(001)$ surface. The adsorption at these sites is a weak physical adsorption except at corner cationic site of $MgO(001)$ surface.
- (2) Strong chemical adsorption for N_2O occurs at

neutral oxygen vacancy site of MgO(001) surface. Especially for N₂O adsorption with O end down, both large adsorption energy and much elongation of N—O bond of N₂O are obtained. MgO(001) surface with oxygen vacancies exhibits high catalysis reactivity toward N₂O adsorptive-decomposition. The large released energy in the dissociation reaction shows that the process of N₂O decomposition is much energetically favorable. On the other hand, from the potential energy surface, it is found that this dissociation process is almost spontaneous. We suggest that not only NO can be converted to N₂O, but N₂O can also be converted to N₂ at neutral oxygen vacancy site, and it is in agreement with the general experimental viewpoint.

(3) MgO(001) surface with magnesium vacancies does not exhibit much reactivity toward N₂O.

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