A Molecular Orbital Study of NO Adsorption on Magnesium Oxide[*]

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The understanding of the mechanisms of the catalytic decomposition and reduction of NO_x is of great importance for solving its pollution. Accordingly there have been interesting experimental investigations on the interactions of nitric oxides with metals or matel oxides. It was found that the chemisorption of NO on MgO powder leads to the decomposition of NO to N_2 and O_2, and/or the formation of N_2O[1,2]. A variety of surface complexes, such as NO^-, NO_2^{2-}, $N_2O_2^{2-}$, and N_2O_2 etc., have been identified by means of ESR and IR measurements under the adsorption conditions[3,4]. At room temperature the NO coverge on MgO (per $Mg^{2+}O^{2-}$ ion pair) is roughly 0.04—0.05[4], imlying that NO chemisorption only occurs at the corner and step sites. However, the mechanism of NO decomposition on metal oxides remains unknown. The present paper covers the results of ab initio calculcations on the interaction between NO and MgO surface.

Table 1   Geometries and binding energies for NO adsorption at Mg_{xC} (x = 3, 4, 5)

Cluster	Site	$R1$/ nm	$R2$/ nm	$R3$/ nm	α	β	Q_{NO}	D_e/ (kJ· mol^{-1})
$(MgO)_4$	Mg_{3C}	0.210 2	0.117 7	0.210 8	60.2	173.1	− 0.29	51
$(MgO)_6$	Mg_{4C}	0.222 1	0.117 1	0.221 1	61.4	168.9	− 0.23	31
$(MgO)_9$	Mg_{5C}	0.266 8	0.115 8	—	45.5	—	0.0	− 5

Solid MgO has a rocksalt structure. We chose the following three cluster models, i.e., $(MgO)_4$, $(MgO)_6$ and $(MgO)_9$ (See Fig. 1 and Fig. 2) to model the different coordinate sites, i.e., Mg_{xC} and O_{yC} (x, y = 3, 4, 5) present on MgO(001) surface. The nearest Mg—O distance was fixed at its bulk value of 0.210 4 nm. A hybrid density functional B3LYP method[5] was used. For O and N, we used the standard 6-31+ G* basis set. For Mg, we used the 6-31G* basis set. For free NO, the N—O bond length optimized with B3LYP method was 0.115 8 nm, in good agreement with the experimental value of 0.115 1 nm.

Two adsorption modes for NO adsorptions at the Mg_{xC} (x = 3, 4, 5) sites of $(MgO)_n$ (n = 4, 6, 9) clusters have been considered, i.e., the N-end down and the O-end down adsorption modes. For the O-end down mode, the interactions between NO and Mg_{xC} (x = 3, 4, 5) were found to be repulsive. For the N-end down adsorption mode, the optimized geome-
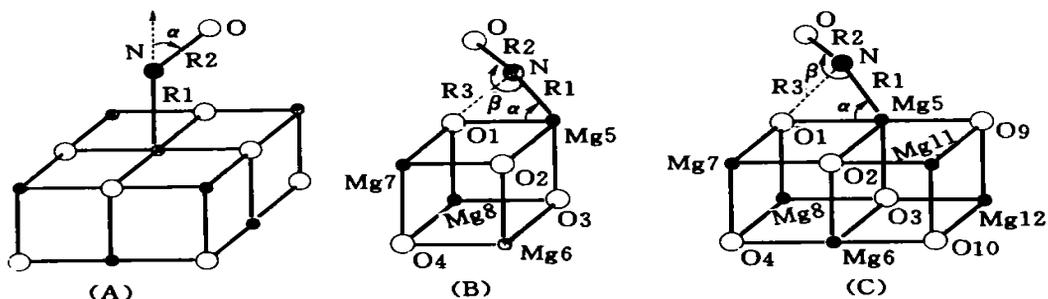

Fig. 1   NO adsorptions at Mg$_{5C}$ on (MgO)$_9$(A), Mg$_{3C}$ on (MgO)$_4$(B) and Mg$_{4C}$ on (MgO)$_6$(C).
All three NO/(MgO)$_n$(n= 4, 6, 9) systems have the C_s symmetry.

tries are presented in Fig. 1, and the optimized geometrical parameters and the corresponding binding energies are listed in Table 1. The binding energies for NO adsorptions at Mg$_{xC}$(x = 3, 4, 5) are 51 kJ/mol, 31 kJ/mol and − 5 kJ/mol, respectively. It is of interest to note that at Mg$_{4C}$ and Mg$_{3C}$, adsorbed NO adopts a geometry with N atom bridging over the Mg—O ion pairs. This kind of geometry favors the formation of two dative bonds, i.e., a donation from the 5σ MO of NO to the empty AO$_s$($3s3p$) of Mg5 atom and a back-donation from the lone pair on O1 atom to the empty $2\pi^*$ MO of NO. This bonding mechanism was further proved by a detailed analysis of the SCF wave function. The ad-species at Mg$_{3C}$, Mg$_{4C}$ were found to be negatively charged, as shown by the calculated natural charges(cf. Table 1). One may have noticed the negative binding energy obtained for NO on Mg$_{5C}$, and may doubt if the negative binding energy is an artifact of the employment of a bared cluster. However, our preliminary embedded cluster model calculation for the NO/(MgO)$_9$ system gave a binding energy as low as 0.4 kJ/mol, indicating that the bonding between NO and a Mg$_{5C}$ terrace site is indeed very weak. It suggests that the adsorption of NO at Mg$_{5C}$ terrace sites on MgO (001) can only occur reversibly at a rather low temperature, while it is impossible at room temperature.

Table 2   Optimized geometries and binding energies for NO adsorption at O$_{yC}$(y= 3, 4)

Cluster	Site	$R1$/ nm	$R2$/ nm	$R3$/ nm	α	β	Q_{NO}	D_e/ (kJ· mol^{-1})
(MgO)$_4$	O$_{3C}$	0. 153 5	0. 130 3	0. 199 1	87. 8	105. 4	− 0. 56	83
(MgO)$_6$	O$_{3C}$	0. 153 5	0. 130 4	0. 198 6	87. 6	105. 5	− 0. 55	84
	O$_{4C}$	0. 152 7	0. 129 1	0. 204 5	88. 9	106. 4	− 0. 69	54

For NO approaching the O$_{yC}$ sites with an O-end down mode, the interactions are repulsive. For NO adsorptions at O$_{yC}$ sites with a N-end down mode, the interaction between NO

Fig. 2   NO adsorption at O$_{3C}$ on (MgO)$_4$(A), O$_{3C}$ on (MgO)$_6$(B) and O$_{4C}$ on (MgO)$_6$(C).
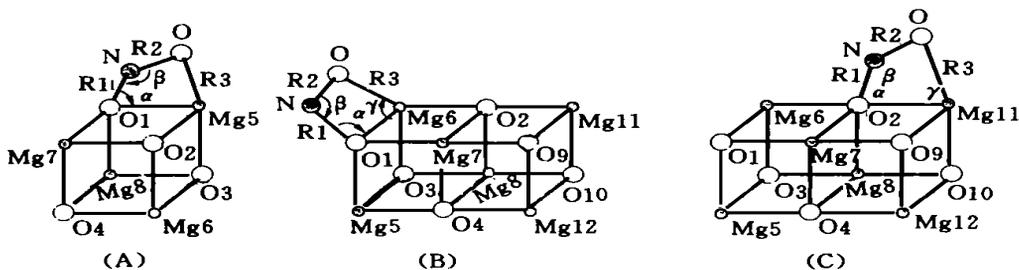
and O_{5C} of $(MgO)_9$ is repulsive, too, while the bondings onto an O_{3C} site and an O_{4C} site are chemisorptive. The optimized geometries of NO adsorptions at the O_{3C} sites of $(MgO)_4$ and $(MgO)_6$, and the O_{4C} of $(MgO)_6$ are presented in Fig. 2, showing a chain-like adsorption configuration. The optimized geometrical parameters and binding energies are given in Table 2. For NO approaching the O_{3C} of $(MgO)_4$ and the O_{3C} of $(MgO)_6$, a rather short intermolecular $N-O_{3c}$ bond length($0.153\ 5$ nm) and a 0.014 nm enlongation of the intramolecular $N-O$ bond length upon adsorption were obtained. The binding energy obtained is 84 kJ/mol. The detailed analysis of the SCF wave function shows that the bonding between NO and the O_{3C} is strongly covalent. These results demonstate that NO is chemisorbed at the O_{3C} sites, and the intramolecular $N-O$ bond is substantially activated upon chemisoption. The same bonding mechanism works for NO adsorption at the O_{4C} of $(MgO)_6$, but with a lower binding energy of 54 kJ/mol.

    We tentatively relate the above theoretical results to the O-exchange reaction between NO and some of the experimental observation available. As cited previously, at room temperature NO can only be adsorbed at the low-coordinate sites located at steps, corners and kinks of MgO crystalline. Our calculations showed that NO can be adsorbed at these sites, either in a bridge configuration or, more preferably, in a chained configuration. With the latter configuration, the chemisorption leads to the formation of a chelated NO_2^{2-} surface species with a coincident activation of the intramolecular $N-O$ bond, as a result, it facilitates O-exchange between NO adspecies and lattice anions. Furthermore, the calculated chemisorption energies of 54—84 kJ/mol for NO at the O_{4C} and O_{3C} sites are in reasonable agreement with the experimentally deduced activation energy of 46 kJ/mol[1] for desorption in the O-exchange reaction.

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