A study of the thermodynamics of surface intermediates formations in the reactions between adsorbed atom and molecules on Pt(111) by the method of BOC-MP

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Abstract

The thermodynamics of $NO_{ad} + H_{ad}$, $NO_{ad} + C_{ad}$, $O_{2,ad} + H_{ad}$ and $C_{2,ad} + H_{ad}$ surface reactions on Pt(111) plane were studied by the method of bond order conservation-morse potential (BOC-MP) analysis. Heats of adsorptions and enthalpies of surface reactions were calculated assuming surface species previously identified by the method of HREELS. It was shown that the formation of 3-atoms intermediates which undergo subsequent reactions are indeed thermodynamically feasible. In a number of cases, the surface intermediate proposed by HREELS had to be slightly modified to make its formation spontaneous. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a recent publication, Smirnov et al. [1] have attempted to elucidate the mechanisms of the formation of surface intermediates in the course of the co-adsorptions of NO + H, NO + C, O_2 + H and C_2 + H on Pt(111) surface where the technique of HREELS have been employed. Such studies are essential in a better understanding of the mechanisms of the reactions of NO + H_2, CO + H_2, etc. The essence of their studies is the detection of adsorbed species and their conversions by the method of HREELS in the temperature range of 100 to 300 K. On this basis, it is concluded that the mechanism involves steps of activation; where atomic H and molecular NO, O_2, C_2 adsorbed species form, synthesis; where three atomic adsorbed intermediates having configuration of η^1 and η^2 form followed by conversion; where subsequent surface reactions and desorption of stable product were observed. On Pt(111) plane, the atomic adsorbates occupy three coordinated hollow sites [2], and they still possess high activities, as HREELS studies revealed this matter by the detection of 3-atomic adsorbed intermediates upon heating the system from 100 to 300 K.

The purpose of the present work has been to apply the method of bond order conservation-morse potential (BOC-MP) analysis [3] to calculate the enthalpies of the adsorbed species and surface reactions in pursuit of the further am-

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plification of the experimental findings by the energetic criteria. We have employed this method to investigate the decomposition routes of NO_2 and $C_2H_5NH_2$, and came up with astonishingly good predictions of products distributions and reaction intermediate justifications over single crystal surfaces of a number of transition metals [4,5].

2. Method

In the method of BOC-MP, the total bond order between the adsorbate and its underlying adsorbent atom(s), is conserved, and the bond energy is assumed to follow the Morse potential model. The optimization of the energy of the adsorbed ensemble, adsorbate and its underlying surface atom(s), is achieved by a variational method [6]. The details of the calculations are explained elsewhere [3,6]. The equations used in this work for the calculations of the heats of adsorptions are given below without going into the details of their derivations. First, the heat of atomic adsorption of A on an n-fold surface site forming M_n–A is

$$Q_A = Q_{0A}(2 - 1/n) \qquad (1)$$

where Q_{0A} is the two center bond energy. For a monocoordinated (η^1) admolecule AB with A end down, M–A–B, three cases have been distinguished. If AB is strongly bonded onto the surface and retains its localized unpaired elec-

Table 1
Presentation of the possible surface species
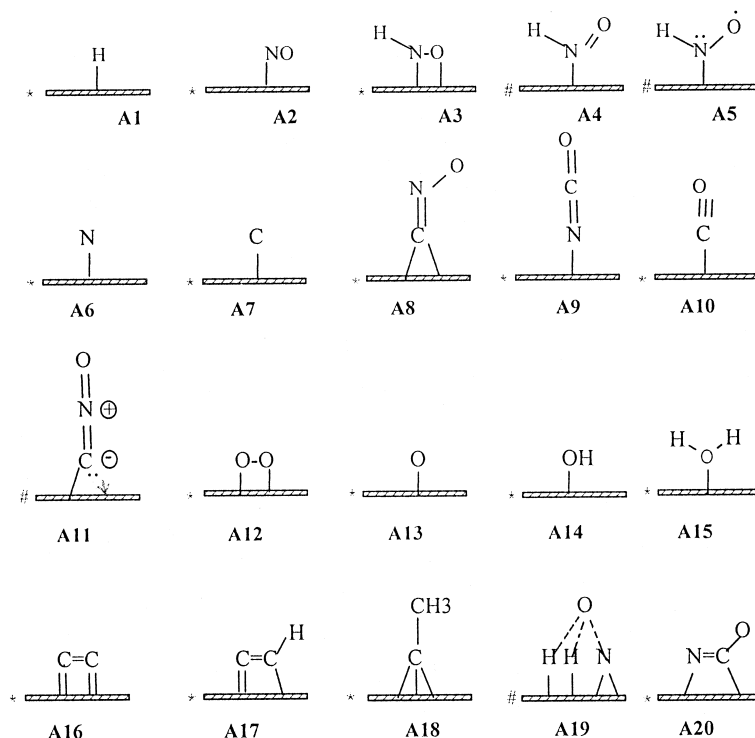
tron as in the case of adsorption of free radicals, one has

$$Q_{AB} = Q_A^2/(Q_A + D_{AB}) \qquad (2)$$

where D_{AB} is the gas phase bond dissociation energy of AB. On the other hand, if AB is weakly bonded onto the surface as in the case of the adsorption of closed shell molecules, one arrives at

$$Q_{AB} = Q_{0A}^2/(Q_{0A} + D_{AB}) \qquad (3)$$

In the intermediate situation, the average of the above values are employed

$$Q_{AB} = 0.5\left\{\left[Q_A^2/(Q_A + D_{AB})\right] \right.$$
$$\left. + \left[Q_{0A}^2/(Q_{0A} + D_{AB})\right]\right\} \qquad (4)$$

For a di-coordinated (η^2) admolecule, where the adsorbed species lie parallel to the surface and forms bonds via both A and B with two surface atoms, heat of adsorption follows

$$Q_{AB} = \left[ab(a + b) + D_{AB}(a - b)^2\right]$$
$$/\left[ab + D_{AB}(a + b)\right] \qquad (5)$$

with

$$a = Q_{0A}^2(Q_{0A} + 2Q_{0B})/(Q_{0A} + Q_{0B})^2 \qquad (5a)$$

$$b = Q_{0B}^2(Q_{0B} + 2Q_{0A})/(Q_{0A} + Q_{0B})^2 \qquad (5b)$$

and in the special case of A_2 adsorption, Eq. (5) simplifies to

$$Q_{A2} = (9/2)Q_{0A}^2/(3Q_{0A} + 8D_{A2}) \qquad (6)$$

The details of the derivations of Eqs. (1)–(6) can be found in the original literature [3,6]. This method provides heats of adsorption and enthalpies of surface reactions [7,8], as well as the activation energies of the formations of surface species and their subsequent reactions [7,8].

3. Results and discussions

Table 1 presents the possible surface species involved in the reactions of $NO_{ad} + H_{ad}$, $NO_{ad} + C_{ad}$, $O_{2,ad} + H_{ad}$ and $C_{2,ad} + H_{ad}$ on Pt(111)

that are either observed by the method of HREELS by Smirnov et al. [1] or speculated. Using Eq. (1)E (2)Eqs. (3)–(6) and the input data, Q values (Q_H, Q_C, Q_O, Q_N), obtained from the literature [7,9,10], the heats of adsorptions of the species presented in Table 1 have been calculated. The gas phase dissociation energies required in the calculations have also been obtained from the literature [11–13]. Table 2 presents the heat of adsorptions (Q), dissociation energies in the gas phase (D) and the total bond energies of the adsorbed species ($Q + D$). The enthalpies of the surface reactions (ΔH) are calculated using Eq. (7) where P_i and R_i refer to the products and reactants respectively, and the results are presented in Figs. 1–4

$$\Delta H = \Sigma\left[(Q + D)_{Pi} - (Q + D)_{Ri}\right] \qquad (7)$$

In Fig. 1a, the enthalpy changes associated with the reactions of $NO + H_2$ resulting surface species proposed in HREELS studies are presented. It is observed that the formation of A3

Table 2
Heat of adsorption (Q), total bond energies in the gas phase (D) and adsorbed state ($Q + D$) on Pt(111) (kcal/mol)

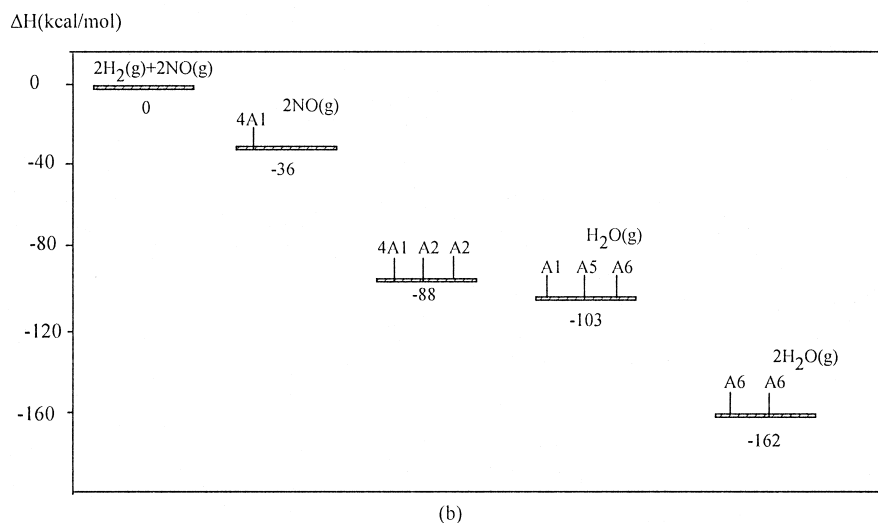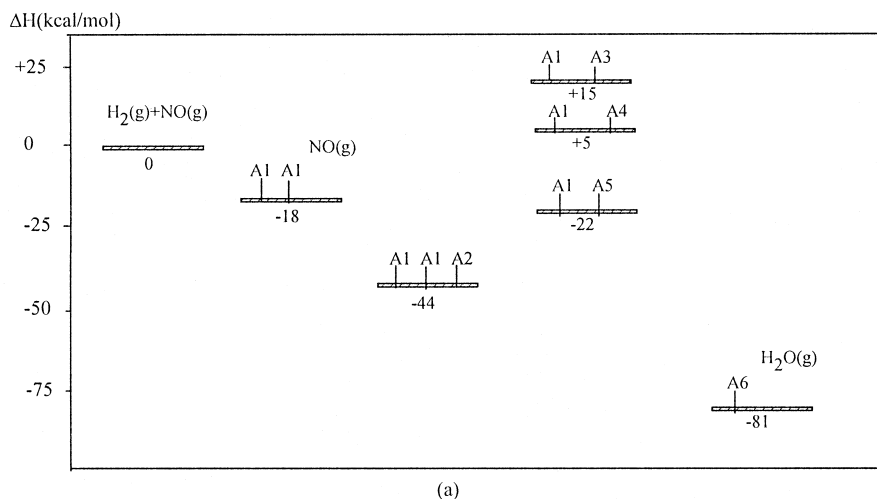| Species	D^a	Q	$Q + D$
A1	–	61	61
A6	–	116	116
A13	–	85	85
A7	–	150	150
$H_2(g)$	104	–	104
NO(g)	151	–	151
$C_2(g)$	178	–	178
$C_2(g)$	119	–	119
A2	151	26	177
A3	169	10	179
A4	169	20	189
A5	169	47	216
A15	220	11	231
A8	185	76	261
A9	325	51	376
A10	257	32	289
A11	267	76	343
A12	119	11	130
A14	102	39	141
A16	178	25	203
A17	259	34	293
A18	376	97	473
A20	325	48	373

[a]Refs. [11–13].

Fig. 1. Presentation of the BOC-MP calculated enthalpy changes in the course of NO + H_2 reaction on Pt(111) exhibiting (a) unfavorable formation of 3-atomic surface species and (b) favorable formation and decomposition of 3-atomic surface moiety.

species is highly unfavored as it is accompanied by a highly positive ΔH. Keeping the 3-atomic structure but varying the electronic structures give rise to entities A4 and A5, which seem to be more favored but still cannot occur on account of the prohibitively positive free energies associated with the process. The entropy changes in the course of surface reactions are normally small, and the free energy is largely controlled by the enthalpy term. However, the energy associated with the simultaneous removal of water

(probably by passing through the transition state A19) and the formation of 3-atomic species can indeed give rise to the spectroscopically verified A5 moiety, Fig. 1b. Fig. 2a presents the enthalpies associated with C + NO reaction. Again, the formation of A8 intermediate as suggested by Smirnov is energetically unfavored. Assuming A11 structure, whose formation is energetically favored and lies between its adsorbed precursor and A9, brings consistency to the pattern of enthalpy changes. In fact, the
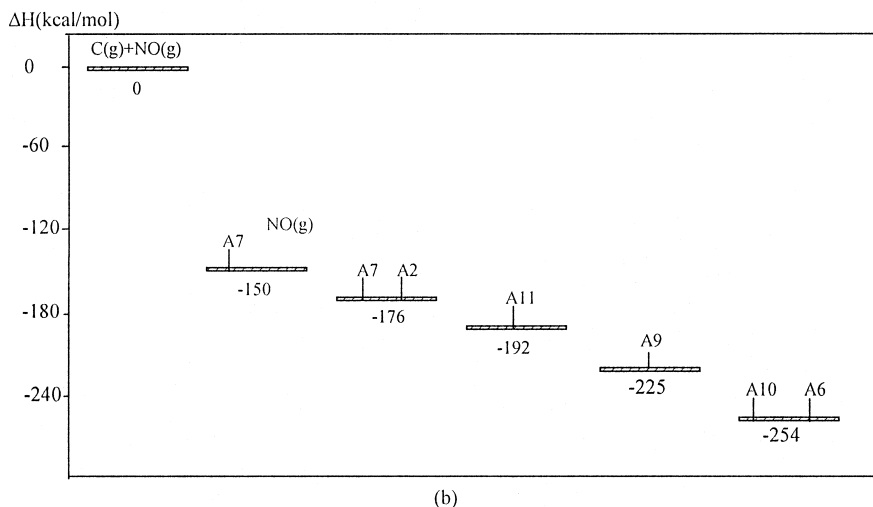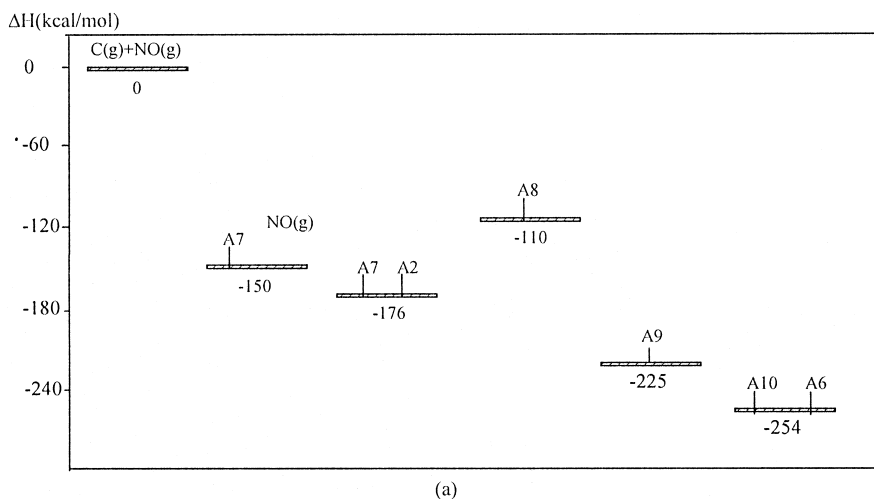
Fig. 2. Presentation of the BOC-MP calculated enthalpy changes in the course of NO + C reaction on Pt(111) exhibiting (a) unfavored formation of A8 and (b) favorable formation of AII surface species.

spectroscopic results are also in support of this assumption. If A8 is to be the intermediate, there should be a peak in the spectrum around 750–850 cm^{-1} due to N–O stretching. This peak has not been observed despite the expansion of the spectrum by a factor of 300 [1]. On the other hand A11 which possesses O=N (or almost a double bond) is expected to show a peak at 1500–1600 cm^{-1} in the loss spectrum [1]. Adsorbed NO also exhibits a peak in this region [1] and after heating to 200 K, a large

peak persists, which can very well be at least partly due to A11. The calculations confirm the rearrangement of CNO to NCO with the structure A9 being slightly more favored over A20. Fig. 3 presents the enthalpy changes in the course of $H_2 + O_2$ reaction on Pt(111), and assuming the same surface species proposed by HREELS studies [1]. An energetically favorable route has been observed. Fig. 4 presents the enthalpy changes in the course of $C_{2,ad} + H_2$ reaction. Our calculations which are based on
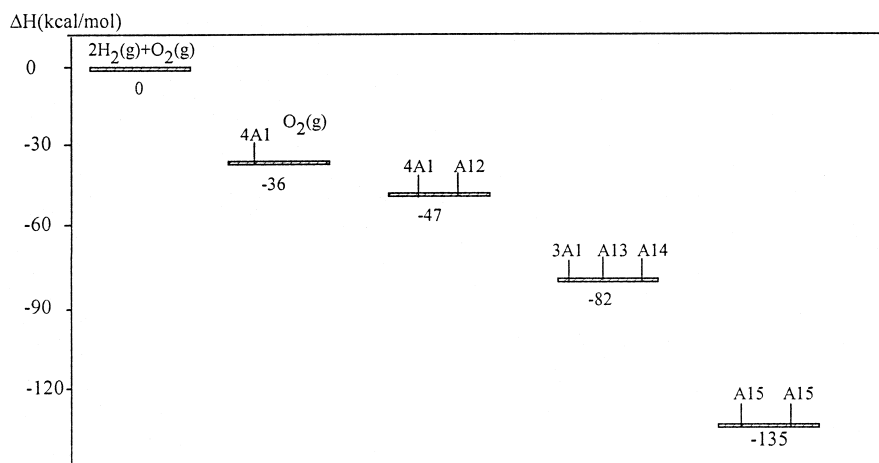
Fig. 3. Presentation of the BOC-MP calculated enthalpy changes in the course of $O_2 + H_2$ reaction on Pt(111).
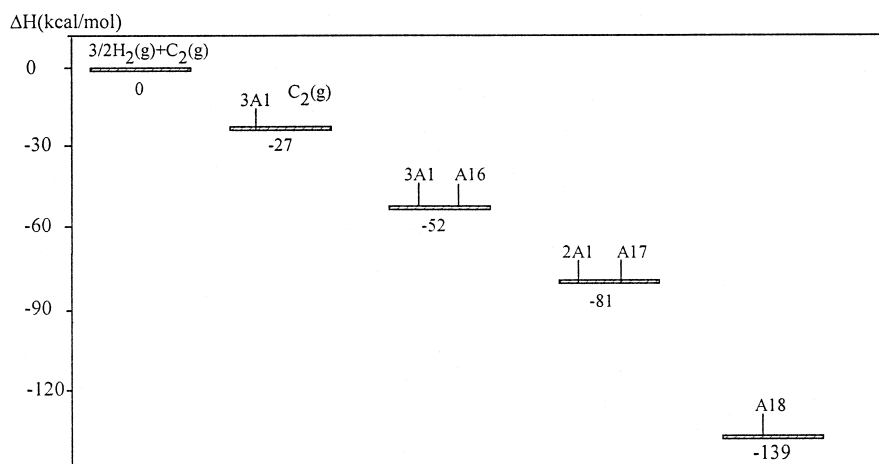

Fig. 4. Presentation of the BOC-MP calculated enthalpy changes in the course of $C_2 + H_2$ reaction on Pt(111).

the existence of the surface species proposed in spectroscopic studies, predict an energetically favorable route.

4. Conclusion

On the basis of this study, it is concluded that energetic criteria in conjunction with spectroscopic measurements can better and less ambiguously propose the routes (intermediates) of heterogeneous catalytic reactions. In this regard, the method of BOC-MP offers both the simplicity and accuracy of the calculations.

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