First-principles analysis of the C-N bond scission of methylamine on Mo-based model catalysts

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First-principles analysis of the C–N bond scission of methylamine on Mo-based model catalysts

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The C–N bond breaking of methylamine on clean, carbon (nitrogen, oxygen)-modified Mo(100) [denoted as Mo(100) and Mo(100)–C(N,O), respectively], Mo₂C(100), MoN(100), and Pt(100) surfaces has been investigated by the first-principles density functional theory (DFT) calculations. The results show that the reaction barriers of the C–N bond breaking in CH₃NH₂ on Mo(100)–C(N,O) are higher than that on clean Mo(100). The calculated energy barrier can be correlated linearly with the density of Mo 4*d* states at the Fermi level after the adsorption of CH₃NH₂ for those surfaces. Moreover, the DFT results show that the subsurface atom, e.g., carbon, can reduce the reaction barrier. In addition, We noticed that the activation energies for the C–N bond breaking on Mo₂C(100) and MoN(100) are similar to that on Pt(100), suggesting that the catalytic properties of the transition metal carbides and nitrides for C–N bond scission of CH₃NH₂ might be very similar to the expensive Pt-group metals. © 2010 American Institute of Physics. [doi:10.1063/1.3292028]

I. INTRODUCTION

The adsorption of amines on metal surface is very important for its implication in catalysis and surface coating chemistry. Methylamine represents the simplest derivative of ammonia. The surface chemistry of molecules containing carbon and nitrogen is interested by the oil industry,¹ but the theoretical investigations about their surface chemistry are relatively few. It is now well established that the transition metal carbides (TMCs) and transition metal nitrides (TMNs) often show more catalytic advantages in the catalytic activity, selectivity, and the resistance to poisoning than their parent metals.^{2,3} In addition, many studies have indicated that the catalytic properties of TMC and TMN are very similar to those more expensive Pt-group metals (Ru, Rh, Pd, Os, Ir, and Pt).^{4,5}

In general, the chemical reactivity of the clean transition metal surfaces will be affected by the surface modification, but the situation maybe confusing a little bit. On the one hand, the most active metals such as Mo are passivated by the carbon or nitrogen or oxygen overlayer. For instances, ammonia is stabilized by the presence of oxygen or carbon on tungsten,⁶ the nitride surface exhibits excellent corrosion resistance,⁷ the activation energy of the C–H bond scission on the W(100)–(5 × 1)–C or W(100)–(2 × 1)–O surface is much larger than that on clean W(100),⁸ and the degree of methylamine dissociation is inhibited by the surface carbon atom left behind the reaction.⁹ In addition, it has been known

that the oxidized Mo(100) surface is less active than the corresponding clean one from the investigation of trimethylamine decomposition.¹⁰ On the other hand, it is usually assumed that the precovered oxygen atom on metal surfaces can enhance the catalytic activity for many other reactions. For example, water molecule dissociation on Cu(111) can be promoted by the precovered oxygen atom, and the similar phenomenon can be found for the reaction of ammonia decomposition on the oxygen-modified Cu(111).¹¹ Therefore intensive theoretical investigations together with the density functional theory (DFT) calculation are helpful. However, despite of many experimental studies for the chemical reactions catalyzed by the TMC, such as Mo₂C, that have been conducted,^{12,13} the theoretical discussion is scarce.²

The adsorption and decomposition of CH₃NH₂ on Mo(100)–c(2 × 2)N (Ref. 9) surface have been studied by using TPD and Auger electron spectroscopy, and the C–N bond cleavage was found. Now, the influence of atomic modification on the activity of Mo(100) and the C–N bond scission of CH₃NH₂ on the clean Mo(100), Mo(100)–C(N,O), Mo₂C(100), MoN(100), and Pt(100) surfaces have been systematically studied using the first principles DFT approach with the slab model in this work. Based on the calculation results, we intend to answer the following questions: (1) What is the reactivity order for the C–N bond scission of CH₃NH₂ on these surfaces? (2) Why are the modified surfaces less efficient for the C–N bond activation of CH₃NH₂ than on the clean surface? (3) Can the TMC and TMN substitute for those more expensive Pt-group metals for C–N bond scission of CH₃NH₂?

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II. COMPUTATIONAL METHOD AND MODELS

All the calculations are performed using the plane-wave DFT (VASP code).^{14,15} The exchange-correlation energy and potential are described by generalized gradient approximation (PW91).¹⁶ The electron-ion interaction is described by the projector-augmented wave scheme,^{17,18} and the electronic wave functions are expanded by plane waves up to a kinetic energy of 315 eV. The lattice parameter of 3.15 Å is used for molybdenum. A periodical four-layer slab representing Mo(100) or Pt(100) is used with ~ 10 Å of vacuum region between slabs. The calculated models are chosen as the unit cells of 2×2 with the corresponding coverage of 1/4 ML. The surface Brillouin zone is sampled using a $4 \times 4 \times 1$ Monkhorst–Pack mesh.¹⁹ The Mo₂C(100) surface was modeled by a four-layer Mo₂C slab using the lattice constants of $a=4.732$ Å, $b=6.037$ Å, and $c=5.204$ Å,²⁰ and the MoN(100) surface was modeled by a four-layer MoN slab using the lattice constants of $a=5.745$ Å and $c=5.622$ Å.²¹ The $4 \times 4 \times 1$ k -point sampling was also used for Mo₂C(100) and MoN(100). During the calculation, the top two layers and the adsorbed species are allowed to be relaxed. The molecules in the gas phase have been calculated using a $15 \times 15 \times 15$ Å³ cubic unit cell. Spin-polarized calculations were performed when needed. The adsorption energy (E_{ads}) of adsorbate is calculated based on the equation of $E_{\text{ads}}(\text{Å}) = E_{\text{A/M}} - E_{\text{M}} - E_{\text{A}}$, where $E_{\text{A/M}}$ refers to the total energy of the adsorbate-substrate system, E_{M} is the total energy of the clean substrate or the one with atomic modifications, and E_{A} denotes the energy of the adsorbate in the gas phase. The minimization of the reaction pathways and the search of the transition states (TSs) have been performed with the climbing-image nudged elastic band method (CI-NEB).²² In this method, a linear path between the reactant and the product states is established as the initial search coordinate. The approximated structures of the TSs are approached by optimizing a set of not less than six intermediate images along that initial coordinate mentioned. Finally, the TSs are identified by exhibiting the existence of a single normal mode associated with a pure imaginary frequency. Then we continued to include the zero point energy (ZPE) into the activation energy.^{23,24}

$$\text{ZPE} = \sum_i (1/2) h \nu_i,$$

where ν_i is the computed real frequencies of the system. To correlate the electronic structure of the surface and its catalytic properties, the d -band center partly describing the electronic effect of the surface, is calculated by the formula^{25,26}

$$\epsilon_d^c = \frac{\int_{-\infty}^{E_f} E \rho_d(E) dE}{\int_{-\infty}^{E_f} \rho_d(E) dE},$$

where ρ_d represents the density of states projected onto the d -band of metal atom and E_f is the Fermi energy. Also, the employed p -band center (ϵ_p^c) is calculated by the similar way.

FIG. 1. Most stable adsorption configurations of CH_3NH_2 , CH_3 , NH_2 , and the TSs of C–N bond breaking of CH_3NH_2 on the clean, C(N, O)-modified Mo(100), Mo₂C(100), MoN(100), and Pt(100) surfaces. [$\text{C}_{\text{(su)}}$ – $\text{C}_{\text{(sb)}}$ denotes the carbon-modified Mo(100) surface with the additional presence of subsurface carbon atom, $\text{C}_{\text{(su)}}$ and $\text{C}_{\text{(sb)}}$ represent the on-surface carbon atom and the subsurface carbon atom, respectively.]

III. RESULTS AND DISCUSSION

A. Adsorption properties of methylamine, methyl, and amino

We first investigated the possible adsorbed species produced in the C–N cleavage of methylamine. Their stable configurations are shown in Fig. 1 and their energetic data are listed in Table I.

1. On the Mo(100)–(C,N,O) surface

We have investigated the possible adsorption sites of methylamine, methyl, and amino on the clean and Mo(100)–C(N,O) surfaces previously.²⁷ Herein, we collect and cite the adsorption energy of most stable adsorption site and the con-

TABLE I. Adsorption of CH_3NH_2 , CH_3 , and NH_2 on the clean, C(N, O)-modified Mo(100), $\text{Mo}_2\text{C}(100)$, MoN(100), and Pt(100) surfaces (unit in eV).

	Mo(100)		Mo(100)–C		Mo(100)–N		Mo(100)–O		$\text{Mo}_2\text{C}(100)$		MoN(100)		Pt(100)	
	E_{ads}	Site	E_{ads}	Site	E_{ads}	Site	E_{ads}	Site	E_{ads}	Site	E_{ads}	Site	E_{ads}	Site
C(N,O)	...	...	−9.20	4h	−7.80	4h	−7.78	4h	...	...	...	...	...	...
CH_3NH_2	−1.12	Top	−1.00	Top	−1.01	Top	−0.98	Top	−0.96	Top	−0.94	Top	−1.05	Top
CH_3	−2.58	Bridge	−2.35	Bridge	−2.30	Bridge	−2.28	Top	−2.77	hcp/fcc	−1.96	Bridge	−2.21	Top
NH_2	−3.97	Bridge	−3.90	Bridge	−3.81	Bridge	−3.55	Bridge	−3.49	hcp	−2.90	Bridge	−3.20	Bri

figuration of the relevant species on the investigated surfaces in Table I and Fig. 1. It turns out that after optimization the preadsorbed atoms (C, N, and O) are all adsorbed on the fourfold hollow site of the Mo(100) surface. Methylamine is adsorbed on the clean and atom modified Mo(100) surface through its nitrogen lone pair electrons in a top configuration. The methylamine adsorption energies are −1.12, −1.00, −1.01, and −0.98 eV on the Mo(100), Mo(100)–C, Mo(100)–N, and Mo(100)–O, respectively. However, methyl is found to be adsorbed in the bridge site on the Mo(100), Mo(100)–C, and Mo(100)–N with the adsorption energy of −2.58, −2.35, and −2.30 eV, respectively. On the Mo(100)–O surface, methyl prefers the top site with the adsorption energy of −2.28 eV. Moreover, the amino is also preferentially adsorbed at the bridge site with the adsorption energy of −3.97, −3.90, −3.81, and −3.55 eV on the Mo(100), Mo(100)–C, Mo(100)–N, and Mo(100)–O, respectively. From the calculation results, we found that the adsorption energies of these radicals at the preferred sites on these surfaces are reduced in the following order: Mo(100) > Mo(100)–C > Mo(100)–N > Mo(100)–O.

2. On the $\text{Mo}_2\text{C}(100)$ and MoN(100) surfaces

The $\text{Mo}_2\text{C}(100)$ consists of alternating Mo and C layers as shown in Fig. 2(a) and it is Mo terminated. The adsorptions of relevant species on $\text{Mo}_2\text{C}(100)$ at the different sites [Fig. 3(a)] were investigated. CH_3NH_2 is adsorbed on the top of Mo, CH_3 positions on the hcp and the fcc sites with the same adsorption energy, and NH_2 prefers the hcp site. In our study, the $\text{Mo}_2\text{C}(100)$ surface has a net dipole and a electrostatic interaction between the slabs can modify the total energy. We checked the effect of dipole on the total energy of the clean slab and on the total energy of adsorption systems of CH_3NH_2 , CH_3 , and NH_2 . Moreover, we found out that the polarity of slab induces the slight increase in total energy for the adsorption system of CH_3NH_2 , CH_3 , NH_2 , and the coadsorption system of CH_3 and NH_2 (data are not shown), but it is neglected for the clean slab. When the polarity correction

FIG. 2. Geometries of $\text{Mo}_2\text{C}(100)$ and MoN(100). Large gray balls denote Mo atoms, small gray balls denote C atoms, and blue balls denote N atoms.

is considered (Table I), the adsorption energies of methylamine, methyl, and amino is −0.96, −2.77, and −3.49 eV, respectively.

The structure of MoN(100) consists of alternating 2Mo–N and N layers, which is shown in Fig. 2(b). We examine the adsorption of CH_3NH_2 , CH_3 , and NH_2 on the top and bridge site of this surface [Fig. 3(b)]. CH_3NH_2 adsorbs on the top site with the adsorption energy of −0.94 eV. CH_3 and NH_2 both chemisorbs preferentially at the bridge site with the adsorption energy of −1.96 and −2.90 eV, respectively.

3. On the Pt(100) surface

On the Pt(100) surface, top, bridge, and fourfold hollow site were considered. CH_3NH_2 prefers the top site with the adsorption energy of −1.05 eV, and CH_3 is also adsorbed on the top site with the adsorption energy of −2.21 eV. However, NH_2 adsorbs on the bridge site with the adsorption energy of −3.20 eV.

B. Methylamine decomposition

After determining the preferred adsorption site for each possible species involved in the processes of methylamine

FIG. 3. Adsorption site of $\text{Mo}_2(100)$ and MoN(100). Large gray balls denote Mo atoms, small gray balls denote C atoms, and blue balls denote N atoms (up: top view; bottom: side view). [The hcp site resides above a subsurface carbon atom in the second substrate layer, and the fcc site resides above a subsurface molybdenum atom in the third substrate layer.]

TABLE II. Energy data of the C–N bond breaking of CH₃NH₂ on the clean, C(N, O)-modified Mo(100), Mo₂C(100), MoN(100), and Pt(100) surfaces. (ΔH is the reaction enthalpy, E_a is the activation energy, the ZPE corrected activation energies are given in parenthesis, and ν_i is the imaginary frequency of the TS.)

	ΔH (eV)	E_a (eV)	ν_i (cm ⁻¹)
Mo(100)	−0.83	1.99(1.75)	538.8i
Mo(100)–C	−0.80	2.28(2.03)	300.3i
Mo(100)–N	−0.63	2.12(1.88)	528.2i
Mo(100)–O	−0.76	2.16(1.93)	544.7i
Mo(100)–p(3 × 2)–C	−0.59	2.06(1.83)	489.6i
Mo(100)–C _(sb)	−1.62	1.18(0.85)	568.7i
Mo(100)–C _(suf) –C _(sb)	−1.16	1.35(1.14)	547.9i
Mo ₂ C(100)	−0.92	2.11(1.93)	706.7i
MoN(100)	−0.24	2.37(2.20)	614.6i
Pt(100)	−0.15	2.36(2.14)	612.3i

decomposition via C–N bond cleavage, we explore the detailed reaction mechanism by the calculations of the activation energy in the following sections. In the initial state (IS), methylamine weakly binds to the surface through its nitrogen atom lone pair electrons on a top site. In the final state (FS), methyl and amino are both adsorbed on their most stable sites. In this work, for a reaction like $AB=A+B$, the calculated total energy change or reaction enthalpy (ΔH) is defined by the formula of $\Delta H=E(A+B)/M-E(AB)/M$, where $E(A+B)/M$ and $E(AB)/M$ are the total energy for the coadsorption system of the product and of the reactant, respectively. Activation energy, E_a , is calculated in terms of equation of $E_a=E_{TS}-E_{(AB)/M}$, where E_{TS} is the total energy of TS. The reaction enthalpy, activation energy, and the geometrical parameters of the TSs are shown in Tables II and III and Fig. 1. We also calculate the ZPE correction for the barriers and list in Table II.

1. On the Mo(100) surface (Ref. 28)

First, the C–N axis of adsorbed methylamine tilts down to the surface. Then, the C–N bond is activated, and breaks down forming two intermediates, methyl and amino radical.

Finally, the methyl is on a bridge site and the amino is on a top site far from the former. From the TS structure (Fig. 1), we can notice that the TS is more productlike, suggesting this is a late-barrier reaction. In the TS, the dissociated CH₃ and NH₂ are both adsorbed on the neighboring top sites with the distance of 2.30 Å. An imaginary frequency of 538.8i cm⁻¹ corresponding to the C–N stretching vibration mode is observed. Thermodynamically, this step is energetically favorable with the overall energy change of −0.83 eV. The calculated reaction barrier is 1.99 eV, and the barrier becomes 1.75 eV when the ZPE correction is included.

2. On the Mo(100)–(C,N,O) surface

On the atom modified Mo(100) surface, the stable ISs and FSs are identified beforehand. In the IS, the methylamine locates on the top site via the nitrogen atom lone pair electrons. The modified atoms such as C, N, and O sit on the fourfold hollow site. In the FS, CH₃ and NH₂ prefer the bridge site, whereas C, N, and O prefer the fourfold hollow site. In all these TSs, CH₃NH₂ has dissociated to CH₃ and NH₂. Moreover, on the Mo(100)–C and Mo(100)–N, the CH₃ and NH₂ fragments are adsorbed on the neighboring top sites, while on the Mo(100)–O, the CH₃ is on the bridge site and the NH₂ is on the nearest top site. The activation energies of C–N bond scission on C, N, and O-modified surfaces are found to be 2.28, 2.12, and 2.16 eV (after the ZPE correction: 2.03, 1.88, and 1.93 eV), respectively. The activation energies are higher on the C(N,O)-modified surfaces than that on the clean Mo(100) surface. This reaction is found to be exothermic by 0.80, 0.63, and 0.76 eV on Mo(100)–C, Mo(100)–N, and Mo(100)–O, respectively, which are more or less lower than that on the clean Mo(100) surface (0.83 eV). In the TS, we observed an imaginary frequency of 300.3i, 528.2i, and 544.7i cm⁻¹ corresponding to the C–N stretching vibration on the Mo(100)–C(N,O), respectively. The properties of the TS are presented in Table III and Fig. 1.

Now the following question gives rise to: why can the preadsorbed atoms (C,N,O) affect the activity of Mo(100)? We carefully looked at the relationship between the adsorption energies of the different preadsorbed atoms on Mo(100) (Table I) and the activation energies, and found interesting

TABLE III. Properties of the TSs of C–N cleavage of CH₃NH₂ on the clean, C(N, O) preadsorbed Mo(100), Mo₂C(100), MoN(100), and Pt(100) surfaces (unit in angstrom).

Metal surface	Preadsorbed atom			CH ₃		NH ₂	
	R _{C–N} ^a	R _{X–Mo} ^b	Site	R _{X–Mo} ^b	Site	R _{X–Mo} ^b	Site
Mo(100)	2.30			3.00	Top	2.05	Top
Mo(100)–C	2.57	0.44	4h	3.21	Top	1.99	Top
Mo(100)–N	2.41	0.43	4h	2.85	Top	2.02	Top
Mo(100)–O	2.49	0.59	4h	2.95	Bridge	2.02	Top
Mo(100)–p(3 × 2)–C	2.36	0.58	4h	3.14	Bridge	2.04	Top
Mo(100)–C _(sb)	1.96	...	...	2.15	Top	2.41	Top
Mo(100)–C _(suf) –C _(sb)	1.91	0.40	4h	2.17	Top	2.31	Top
Mo ₂ C(100)	1.95	...	...	2.69	Top	2.20	hcp
MoN(100)	2.06	...	...	2.81	Top	2.15	Bridge
Pt(100)	2.13	...	...	2.23	Top	1.99	Top

^aR_{C–N} represents the distance between CH₃ and NH₂.

^bX represents the preadsorbed surface atom, CH₃, and NH₂, respectively.

FIG. 4. Linear relationships between the reaction barrier of the C–N bond cleavage of CH_3NH_2 and the adsorption energy for the different modified atoms (C, N, and O) on Mo(100) (a), and the projected density of the Mo 4d states at Fermi level for the $\text{CH}_3\text{NH}_2/\text{Mo}$ and $\text{CH}_3\text{NH}_2/\text{Mo}(100)\text{-X}$ systems ($\text{X}=\text{C}$, N, and O) (b).

result [Fig. 4(a)], that shows that the adsorption energy of the preadsorbed atom is varied opposite to the variation in chemical activity of the corresponding atom modified surfaces (i.e., the greater the adsorption energy, the less active the metal surface). Here, we should note that the activation energies used in all the analyses in this paper, including the linear regression and the decomposition of activation energy, are those without the ZPE correction, because it is tested that the qualitative linear regression results are the same with or without the ZPE correction. Obviously, the more strongly the modified atoms bound to the metal Mo, the more passivating effect they have on the methylamine C–N bond cleavage. This conclusion is in agreement with our previous result that the promotion effect of preadsorbed atom for the water dissociation is also related to its adsorption strength.^{29,30}

Cao and Chen³¹ investigated the adsorption and decomposition of water on clean and atom (C,N,O) contaminated Pd(111) surface, where the preadsorbed atoms participate in the reaction and abstract the hydrogen atom from the water. As it has been reported that the DOS at the Fermi level governs reactivity of a species,^{32,33} they correlated the barrier with the Fermi-energy projected density of states (PDOS) of the preadsorbed atoms 2p orbital after the adsorption of water, and found a very nice linear relationship. In our present work, the preadsorbed atom only acts as the “spectator” in the C–N bond cleavage of CH_3NH_2 , and the activity differ-

ence of the atom modified surfaces is mainly determined by the PDOS of Mo 4d states at the Fermi level. One may expect that there is a correlation between the reaction barrier and the Mo 4d PDOS at the Fermi level. The Mo 4d density of states at the Fermi level, on the clean and C(N,O) modified Mo(100) surfaces, $N(E_F)$, are 2.58, 2.09, 2.30, and 2.27 states/eV/atom after the CH_3NH_2 adsorption, respectively. Indeed, we found a very nice linear relationship between these two quantities of the four systems [Fig. 4(b)].

Besides the relationships between the reaction barrier and the adsorption energy of the preadsorbed atoms, and the Mo 4d PDOS at the Fermi-level, we also analyzed the relationship between the reaction barrier and the 2p-band center variation of the preadsorbed atoms, with and without the adsorption of CH_3NH_2 . Before the adsorption of CH_3NH_2 , the 2p-band center of the modifiers for the C(N,O)-modified Mo(100) surfaces is -3.55 , -4.40 , and -5.47 eV, respectively. After the adsorption of CH_3NH_2 , the 2p-band center of the modifiers is -3.78 , -4.43 , and -5.61 eV, respectively, that downshift the 2p-band center (-0.23 , -0.03 , and -0.14 eV) of the modifiers for the C(N,O)-modified surfaces. And a clear linear relationship between these two quantities was found [Fig. 5(a)]. It is obvious that a large downshift of the 2p-band center induced by the adsorption of methylamine and the higher reaction barrier induced by the

FIG. 5. Linear relationships between the reaction barrier and the shift of 2p-band center of modified atoms (X) at the most stable configuration of CH_3NH_2 adsorption. (a) $\text{X}=\text{C}$, N, and O ($\theta=1/4$); and (b) $\text{X}=\text{C}$ ($\theta=1/4$, $\theta=1/6$, C_{sb} , and $\text{C}_{suf}-\text{C}_{sb}$).

modification of atom are resulted from a common reason, i.e., the competition in the adsorptions of C(N,O) and CH₃NH₂.

High-resolution electron energy loss spectroscopy experiments³⁴ showed that the CH₃ group is bound to the surface Mo atoms rather than the surface oxygen during the adsorption of methyl on the oxygen-modified Mo(100) surface, so the nonmetal components only play the electronic effect and does not participate in C–N bond cleavage. In fact, it is difficult to tell the difference between ligand effect and ensemble effect.³⁵ Our DFT calculations show that the Mo surface becomes less open in the presence of the surface modified atoms such as carbon as compared to the pure Mo(100), which may result in the deactivation of surface Mo atom. This may be one kind of “ensemble effect” or “strain effect.”³⁶ When the reactants and products are located on the top of the nonmetal components initially, and the nonmetal components will adsorb the reactants and products, which disagree with the experiment result. In order to investigate the effect of the nonmetal components on the dehydrogenation of methylamine, we investigated the C–H bond breaking on the clean and nitrogen atom modified Mo(100) surfaces using the unit cells of p(2×2) with the coverage of 1/4 ML. The barriers are 0.56 and 1.66 eV on clean and nitrogen atom modified Mo(100) surfaces, which indicates that the presence of nitrogen atom inhibits the dehydrogenation of methylamine.

The calculation results are in general agreement with the experimental observations that the activation energy of C–H bond scission on the W(100)-(5×1)-C or W(100)-(2×1)-O surface was much larger than that on clean W(100),⁸ and they are also consistent with the general experimental conclusion that the high reactivity of Mo(100) surface will be “tamed” by the formation of carbide.¹⁰ Moreover, the increased energy barrier of C–N bond scission on the oxygen atom precovered Mo(100) may suggest that the precovered oxygen atom act as a poison rather than a promoter, which is very different from the case of the precovered O on the Cu metal and other less active metals.³⁰ The possible reason is that the adsorption of oxygen atom on Mo(100) is too strong to active the C–N bond of CH₃NH₂, namely, the adsorbed oxygen atom may block the surface active site. On the Cu(111), however, the weakly adsorbed oxygen has the ability to promote the O–H bond breaking of H₂O, because it forms the H-bonding with the adsorbed H₂O facilitating the breakage of O–H bond.

3. Surface coverage effect

In order to investigate the effect of surface coverage on the C–N activation, we study the coverage of 1/6 and 1/4 ML. And a p(3×2) model is employed for the 1/6 ML Mo(100)–C surface. In the IS, methylamine is on the top site through the nitrogen lone pair and the precovered carbon atom is on the fourfold hollow site. In the FS, the CH₃ prefers the bridge site and the NH₂ is on another bridge site about 5 Å away. However, in the TS, there is an imaginary frequency of 489.6i cm^{−1} corresponding to the C–N stretching vibration, and the dissociated CH₃ and NH₂ are adsorbed on the nearest bridge site and top site, respectively, with the

C–N length of 2.36 Å. The reaction is exothermic by 0.59 eV and the ZPE included barrier of this path is 1.83 eV. Compared with previous result at higher coverage ($\theta=1/4$ ML), the barrier (1.83 eV) is clearly decreased.

In addition, we also investigated the C–N bond breaking of methylamine occurred on the nitrogen atom modified Mo(100) surface using the unit cells of p(2×2) with the coverage of 1/2 ML. The barrier is 2.41 eV, which is higher than that of 2.12 eV at the 1/4 ML coverage. It is assumed that the higher coverage the preadsorbed atom, the more passivated effect.

4. Subsurface atom effect

Strictly speaking, the differences in the activation energies on C(N,O) preadsorbed surfaces are not more than 0.2 eV for the C–N bond cleavage on those Mo(100) surfaces (Table II), indicating the induced deactivation effects almost the same, which is consistent with the theoretical investigation that the C and N in MoC and MoN have approximately equally electronic effects on Mo.² In addition, the on-surface adsorbed atoms behave entirely different from the corresponding subsurface inserted atoms. Chen³⁷ has shown that the decomposition of unsaturated hydrocarbons on the carbon-modified Mo(110) surface, terminated by carbon atoms, is deactivated, while the surface with carbon atoms into the subsurface region is facilitated. Xu *et al.*³⁸ have also reported that the subsurface oxygen markedly increased the reactivity of Ag(111), and proposed that the subsurface oxygen atom may have the relatively weak binding energy, so the higher promoter effect may be expected. In this contribution, we demonstrate the dramatic effect of subsurface carbon atom (C_(sb)) on the catalytic activity of Mo(100) and Mo(100)–C surfaces, in particular, answer the question of how does C_(sb) modify both the adsorption of methylamine (methyl, amino) and the dissociation of methylamine?

a. The effect of the subsurface carbon atom (C_(sb)). We first study the effect of the subsurface carbon atom on the dissociation of methylamine. The adsorption energies of methylamine, methyl, and amino are calculated with the 1/4 ML coverage of C_(sb). We investigate the adsorption on the top site for the methylamine and on the top, bridge, and fourfold hollow site for the methyl (amino). The adsorption energy of methylamine is −1.62 eV. It is larger than that of −1.12 eV without the presence of C_(sb). Methyl and amino are both stabilized on the bridge site with the adsorption energies of −3.38 and −4.79 eV, larger than that of −2.58 and −3.97 eV without the presence of C_(sb), respectively. After determined the most stable adsorption configuration for each species, the reaction path linking to the C–N bond activation was explored by the nudged elastic band method. The stable configurations of the methylamine, methyl, amino, and the TS are shown in Figure 1. Compared with the case without C_(sb), the introducing of C_(sb) reduces the reaction barrier from 1.75 to 0.85 eV, after ZPE correction. Here, the TS is identified by an imaginary frequency of 568.7i cm^{−1}. The length of C–N bond in TS is 1.96 Å. In the TS, CH₃NH₂ has been dissociated into CH₃ and NH₂, residing on the nearest

FIG. 6. Linear relationships between the reaction barrier and the shift of 2p-band center of modified atoms (X) at the TS. (a) X=C, N, and O ($\theta=1/4$); and (b) X=C ($\theta=1/4$, $\theta=1/6$, C_(sb), and C_(suf)-C_(sb)).

two top sites.

Now we will explain the promotion effect of subsurface carbon atom from both electronic and geometric effects. For the former case, the *d*-band center calculation results show that both subsurface carbon atom and the surface carbon atom withdraw electrons from Mo and deactivate the metal in spite of little difference between them (−2.08 eV versus −1.94 eV), so the electronic effect can not explain the promotion effect of the subsurface carbon atom. For the geometric effect, we found that the top layer becomes more open as compared to the case of pure Mo(100) due to the existing of the subsurface carbon atom, so it is expected that the surface molybdenum atom will have higher activity [this can be further confirmed by the relatively larger adsorption energy on subsurface atom modified Mo(100)]. So subsurface carbon behaves differently from the one on the surface and it helps the C–N bond cleavage. Based on the above discussion, it seems the geometric effect may be the domination one to control the chemical activity in the subsurface carbon atom modified Mo(100).

b. The coefficient of subsurface and on-surface carbon atom (C_(sb)+C_(suf)). In this section we investigate the effect of subsurface carbon atom with the presence of on-surface carbon on the dissociation of methylamine. We consider the case of one on-surface carbon atom in the fourfold hollow site plus one subsurface carbon atom, i.e., a total coverage of 0.50 ML. We investigate the adsorption on the top site for the methylamine and on the top and bridge sites for the methyl (amino). From the calculated results, we find that the adsorption energy of methylamine is −1.22 eV. It is smaller than that of −1.62 eV with only the presence of subsurface carbon atom, but larger than that of −1.00 eV with only the presence of on-surface carbon atom. Methyl and amino are both unstable on the top site and move to the bridge site during the optimization with the adsorption energy of −2.46 and −4.11 eV. They are smaller than the case with only the presence of subsurface carbon atom (−3.38 and −4.79 eV for methyl and amino, respectively), but larger than that of −2.35 and −3.90 eV with only the presence of on-surface carbon atom for methyl and amino, respectively. The stable configurations of the methylamine, methyl, amino, and the TS of the C–N breaking are shown in Fig. 1. The reaction

barrier including ZPE is 1.14 eV, which is larger than that of 0.85 eV with the subsurface carbon atom alone, but it is smaller than that of 2.03 eV with the on-surface carbon atom alone. The TS is still identified by an imaginary frequency of 547.9i cm^{−1}. The length of C–N bond in TS is 1.91 Å. In the TS, CH₃NH₂ has been dissociated into CH₃ and NH₂, sitting on the nearest two top sites.

Similar to the precovered atom modified Mo(100) surfaces, we also expect there is a relationship between the C–N bond broken barrier and the variation of on-surface C atom 2p-band center at the most stable adsorption configuration for the four carbon-modified Mo(100) surfaces [i.e., Mo(100)–C, Mo(100)–p(3×2)–C, Mo(100)–C_(sb), and Mo(100)–C_(suf)–C_(sb)] [see Fig. 5(b)]. At the same time, a nearly linear correlation between energy barrier and the variation of modifiers 2p-band center at the TS is also observed (Fig. 6).

5. On the Mo₂C(100) and MoN(100) surfaces

In this section, we take the activation of C–N bond in CH₃NH₂ on the Mo₂C(100) and MoN(100) surfaces as an example to study the reaction on the real catalysts. On the Mo₂C(100) surface, the C–N cleavage starts with the elongate of the C–N bond in CH₃NH₂ adsorbed on the top site, and completes with the two different location of CH₃ and NH₂. In the two FSs, the NH₂ both sits on the hcp site, whereas the CH₃ locates on the hcp site or fcc site. For these two reaction paths, the calculated total energy change, activation energy and the character of the TS are similar to each other. So, we take the case of CH₃ and NH₂ both locating on the hcp site in the FS as an example to describe the C–N bond breaking on the Mo₂C(100). The calculated activation energy without the ZPE correction is 2.11 eV. In the TS, the methylamine has dissociated into CH₃ and NH₂. CH₃ and NH₂ are adsorbed on the top site and neighboring hcp site, respectively, with the distance of 1.95 Å. There is an imaginary frequency of 706.7i cm^{−1} corresponding to the C–N stretching vibration. The reaction is exothermic by 0.92 eV.

On the MoN(100) surface, the reaction also takes place on the top site. In the FS, the CH₃ prefers the off-top site and the NH₂ is on the bridge site about 3 Å away. In the TS, the dissociated CH₃ and NH₂ are adsorbed on the top site and the

TABLE IV. Energy decomposition of the calculated activation energy. [All of the energies are in eV. Values in parentheses are the contribution of the respective component to the activation energy with respect to the clean Mo(100) surface. Positive (negative) values indicate the component increases (decreases) the reaction barrier relative to the clean surface.]

	ΔE_{sub}	$\Delta E_{\text{CH}_3\text{NH}_2}^{\text{def}}$	$-E_{\text{CH}_3\text{NH}_2}^{\text{IS}}$	$E_{\text{CH}_3}^{\text{TS}} + E_{\text{NH}_2}^{\text{TS}}$	$E_{\text{CH}_3}^{\text{TS}}$	$E_{\text{NH}_2}^{\text{TS}}$	$E_{\text{CH}_3 \cdots \text{NH}_2}^{\text{int}}$
Mo(100)	0.13	2.86	1.04	-4.16	-0.90	-3.26	2.11
Mo(100)-C	0.18(0.05)	3.53(0.67)	1.06(0.02)	-3.53(0.63)	-0.34(0.56)	-3.19(0.07)	1.04(-1.07)
Mo(100)-N	0.22(0.09)	3.23(0.37)	1.05(0.01)	-4.08(0.08)	-0.87(0.03)	-3.21(0.05)	1.69(-0.42)
Mo(100)-O	0.20(0.07)	3.24(0.38)	1.01(-0.03)	-4.17(-0.01)	-0.80(0.1)	-3.37(-0.11)	1.88(-0.23)
Mo(100)-p(3 × 2)-C	0.09(-0.04)	2.95(0.09)	1.10(0.06)	-3.99(0.17)	-0.61(0.29)	-3.38(-0.12)	1.90(-0.21)
Mo(100)-C _(sb)	0.02(-0.11)	1.63(-1.23)	1.17(0.13)	-5.95(-1.79)	-2.05(-1.15)	-3.90(-0.64)	4.31(2.20)
Mo(100)-C _(suf) -C _(sb)	0.25(0.12)	2.27(-0.59)	0.93(-0.11)	-5.49(-1.33)	-2.35(-1.45)	-3.14(0.12)	3.39(1.28)

neighboring bridge site with the C-N length of 2.06 Å. There is an imaginary frequency of 614.6i cm⁻¹ corresponding to the C-N stretching vibration. The reaction is exothermic by 0.24 eV and the barrier without the ZPE correction is 2.37 eV. Compared with previous result on Mo(100) (1.99 eV), the barriers on Mo₂C(100) (2.11 eV) and MoN(100) (2.37 eV) surfaces are clearly increased. This indicates that the reactivities of Mo₂C(100) and MoN(100) are lower than the Mo(100), which can be attributed to the downshift of *d*-band center [-1.77, -3.05, and -3.43 eV for Mo(100), Mo₂C(100), and MoN(100), respectively].

For Mo₂C(100) surface, subsurface carbon also presents, however, the barrier of C-N bond breaking is very high. This can be attributed to the openness of the top metal layer. For the Mo₂C(100) surface, the distance between two metallic Mo atoms on the top layer is only ~3.0 Å, which is much smaller than the case of subsurface carbon atom modified Mo(100) (the distance between two metallic Mo atoms on the top layer in the range of ~3.15–3.20 Å). This may reduce the activity of Mo atom. More importantly, the *d*-band center of metallic Mo on Mo₂C(100) is far from the Fermi level compared to the pure Mo atom (-3.05 eV versus -1.77 eV), and this may be the main factor controlling the chemical activity.

6. On the Pt(100) surface

As mentioned in the introduction, the catalytic properties of TMC and TMN are very similar to those of more expensive Pt-group metals. To compare with the activity of TMC and TMN for methylamine decomposition via C-N cleavage, a Pt(100)-p(2 × 2) model with the coverage of 1/4 ML was used to study the activation of C-N bond in CH₃NH₂. The calculated activation energy without the ZPE correction is 2.36 eV, which is slightly higher than the result of 2.11 eV on the Mo₂C(100), and it is similar to the result of 2.37 eV on the MoN(100). In the TS, the methylamine has dissociated into CH₃ and NH₂. Both CH₃ and NH₂ are adsorbed on the neighboring top sites with the distance of 2.13 Å. There is an imaginary frequency of 612.3i cm⁻¹ corresponding to the C-N stretching vibration. The reaction is exothermic by 0.15 eV.

7. Barrier decomposition

To look further insight into the physical origin of the barrier, we decompose the calculated barrier using the following formula:³¹

$$E_a = \Delta E_{\text{sub}} + \Delta E_{\text{CH}_3\text{NH}_2}^{\text{def}} - E_{\text{CH}_3\text{NH}_2}^{\text{IS}} + E_{\text{CH}_3}^{\text{TS}} + E_{\text{NH}_2}^{\text{TS}} + E_{\text{CH}_3 \cdots \text{NH}_2}^{\text{int}},$$

where $\Delta E_{\text{sub}} = E_{\text{sub}}^{\text{TS}} - E_{\text{sub}}^{\text{IS}}$, reflects the influence of the structural change of the substrate from IS to TS on the activation energy. $\Delta E_{\text{CH}_3\text{NH}_2}^{\text{def}} = E_{\text{CH}_3 \cdots \text{NH}_2}^{\text{gas}} - E_{\text{CH}_3\text{NH}_2}^{\text{gas}}$, is named as deformation energy, which measures the effect of the structural deformation of CH₃NH₂ on the barrier. $E_{\text{CH}_3\text{NH}_2}^{\text{IS}}$ is the adsorption energy of CH₃NH₂ in the IS configuration, $E_{\text{CH}_3}^{\text{TS}}$ and $E_{\text{NH}_2}^{\text{TS}}$ are the adsorption energies of CH₃ (without NH₂) and NH₂ (without CH₃) in the geometry of the TS, respectively. $E_{\text{CH}_3 \cdots \text{NH}_2}^{\text{int}}$ is the interaction between CH₃ and NH₂ in the TS, including the Pauli repulsion^{39,40} between CH₃ and NH₂ and the bonding competition effects^{41,42} caused by sharing the same substrate atom between CH₃ and NH₂.

We collected the contributions to the activation energy of each term in Table IV. From the results, we can see that ΔE_{sub} on the atom modified Mo(100) surface is a little larger than that of the clean Mo(100) except for the Mo(100)-p(3 × 2)-C and Mo(100)-C_(sb) surface, which indicates a slight increase in the energy barrier. The $\Delta E_{\text{CH}_3\text{NH}_2}^{\text{def}}$ can be characterized by the distance between carbon and nitrogen (*R*_{C-N}) of the CH₃NH₂ in TS (Table III and Fig. 1). From Fig. 1, it is clear that the *R*_{C-N} increases with the order of

$$\begin{aligned} \text{Mo(100)} \quad (2.30 \text{ \AA}) &< \text{Mo(100)-p(3 \times 2)-C} \quad (2.36 \text{ \AA}) \\ &< \text{Mo(100)-N} \quad (2.41 \text{ \AA}) \\ &< \text{Mo(100)-O} \quad (2.49 \text{ \AA}) \\ &< \text{Mo(100)-C} \quad (2.57 \text{ \AA}) \end{aligned}$$

which is consistent with the order of $\Delta E_{\text{CH}_3\text{NH}_2}^{\text{def}}$. For the Mo(100)-C_(sb) and Mo(100)-C_(suf)-C_(sb) surface, *R*_{C-N} is decreased compared with Mo(100), which is consistent with the decrease in the $E_{\text{CH}_3\text{NH}_2}^{\text{def}}$. For the investigated surfaces, the difference of $E_{\text{CH}_3\text{NH}_2}^{\text{IS}}$ (~0.20 eV) is small relative to the difference of barriers. From the sum $E_{\text{CH}_3}^{\text{TS}} + E_{\text{NH}_2}^{\text{TS}}$, one can explain why the Mo(100)-C_(sb) is the best catalyst. The dif-

FIG. 7. Linear relationships between the reaction barrier and $E_{CH_3}^{TS}$ (a), $E_{CH_3 \cdots NH_2}^{int}$ (b) or R_{C-N} (c). [a=Mo(100)–C; b=Mo(100)–N; c=Mo(100)–O; d=Mo(100)–p(3×2)–C; e=Mo(100)–C_(sb); and f=Mo(100)–C_(surf)–C_(sb).]

ference of $E_{NH_2}^{TS}$ is small between these different surfaces, and thus has small effect on the energy barrier. From the data of $E_{CH_3}^{TS}$, we find that most of the values in parentheses are positive, which indicate that in most cases the attractive interactions of CH₃ with the substrate are decreased by the modification, except for the cases of Mo(100)–C_(sb) and Mo(100)–C_(surf)–C_(sb). And a moderate linear correlation was observed between the barrier and $E_{CH_3}^{TS}$ [Fig. 7(a)]. Moreover, the absorbed strength of CH₃ at TS ($E_{CH_3}^{TS}$) can be further confirmed by its electronic densities at the Fermi level, $N(E_f)$, that is, 0.30, 0.62, 0.30, and 0.29 states/eV/atom on the clean and C(N, O)-modified Mo(100) surfaces, respectively, which is qualitatively consistent with the $E_{CH_3}^{TS}$ listed in Table IV [–0.90 eV (clean), –0.34 eV (C), –0.87 eV (N), and –0.80 eV (O), respectively], and is qualitatively consistent with the adsorption energy of the precovered atoms listed in Table I [–9.20 eV (C), –7.80 eV (N), and –7.78 eV (O), respectively]. What more interesting is that for the interaction energy of the TS, $E_{CH_3 \cdots NH_2}^{int}$, we find clear linear relationships between the activation energy and the $E_{CH_3 \cdots NH_2}^{int}$ as well as the distance between CH₃ and NH₂ (R_{C-N}) [Figs 7(b) and 7(c)]. $E_{CH_3 \cdots NH_2}^{int}$ has a negative correlation to the activation energy, that is, larger Pauli repulsion means a lower energy barrier. Therefore, based on the above analysis, it seems that both $E_{CH_3}^{TS}$ and $E_{CH_3 \cdots NH_2}^{int}$ could be two of the most important factors related to the variation of activation energy.

IV. CONCLUSION

In summary, this work represents a systematic theoretical study on the methylamine decomposition through the C–N bond cleavage on the clean Mo(100), Mo(100)–C(N,O), Mo₂C(100), MoN(100), and Pt(100) surfaces. Firstly, DFT calculations show that the activation energy of C–N bond cleavage is increased on the C(N,O)-modified Mo(100). Namely, the transition metallic Mo surface is deactivated by the preadsorbed (C,N,O) atoms which has been experimentally observed. It may be due to that these more electronegative atoms reduce the electron donation from the metal to the adsorbates, which can be seen from the density of states of the Mo 4d states at the Fermi level after the adsorption of CH₃NH₂. Secondly, it is found that the surface coverage can affect the activation energy, and the barrier reduces with the decrease of coverage of preadsorbed atom. Thirdly, the subsurface carbon atom has a dramatic effect on the catalytic activity of catalyst. When only the subsurface atom is present, the activation energy is lower than that on the clean surface. When the subsurface and the surface atoms are both present, the activation energy is in the middle of the presence of subsurface carbon atom alone and the presence of surface carbon atom alone. These findings suggest that the preadsorbed impurities (carbon, nitrogen, and oxygen) play an important role on the early transition metal catalysts. Fourthly, the methylamine decomposition on the Mo₂C(100) and MoN(100) surfaces are difficult than on the Mo(100) surface, which indicate that the reactivities of Mo₂C(100)

and MoN(100) are lower than the Mo(100). Furthermore, one could envision using the TMC and TMN to replace those more expensive Pt-group metals for C–N bond scission of methylamine, which has here been verified on the Mo₂C(100), MoN(100), and Pt(100) surfaces.

At last, it is necessary to point out that we only study the C–N bond broken in CH₃–NH₂ in this work, and do not consider other possible steps including the C–N bond broken. For example, Johnson *et al.*⁴³ have studied the adsorption and decomposition of methylamine on Ru(001) using high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry. They found that the majority decomposition pathway available to irreversibly adsorbed methylamine is complete dehydrogenation to chemisorbed CN. The intermediate which precedes C–N bond cleavage is bridging methyleniminium, μ - η^2 -H₂CNH₂. Herein, we have also studied the reactions of CH₃NH₂ → CH₂NH₂+H and CH₂NH₂ → CH₂+NH₂ on Mo(100) and Mo(100)–N. For CH₃NH₂ → CH₂NH₂+H, the barriers are 0.56 and 1.66 eV on Mo(100) and Mo(100)–N. For CH₂NH₂ → CH₂+NH₂, the barriers are 0.86 and 1.17 eV on Mo(100) and Mo(100)–N. We will investigate the different C–N bond breaking paths in our further study.

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