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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 4d 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, 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. 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).

In general, the chemical reactivity of the clean transition metal surfaces will be affected by the surface modification, but the situation may confuse 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 instance, ammonia is stabilized by the presence of oxygen or carbon on tungsten, the nitride surface exhibits excellent corrosion resistance, 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), and the degree of methylamine dissociation is inhibited by the surface carbon atom left behind the reaction. 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. 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). 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, the theoretical discussion is scarce.

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?
II. COMPUTATIONAL METHOD AND MODELS

All the calculations are performed using the plane-wave DFT (VASP code).\textsuperscript{14,15} The exchange-correlation energy and potential are described by generalized gradient approximation (PW91).\textsuperscript{16} The electron-ion interaction is described by the projector-augmented wave scheme,\textsuperscript{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 $2 \times 2$ with the corresponding coverage of 1/4 ML. The surface Brillouin zone is sampled using a 4\times4\times1 Monkhorst–Pack mesh.\textsuperscript{19} The Mo$_2$C(100) surface was modeled by a four-layer Mo$_2$C slab using the lattice constants of $a=4.732$ Å, $b=6.037$ Å, and $c=5.204$ Å,\textsuperscript{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.\textsuperscript{21} The 4\times4\times1 $k$-point sampling was also used for Mo$_2$C(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 Å$^3$ cubic unit cell. Spin-polarized calculations were performed when needed. The adsorption energy ($E_{\text{ads}}$) of adsorbate is calculated based on the equation of $E_{\text{ads}}(A) = E_{A/M} - E_M - E_A$, where $E_{A/M}$ 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).\textsuperscript{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 a single existence of any mode associated with a pure imaginary frequency. Then we continued to include the zero point energy (ZPE) into the activation energy\textsuperscript{23,24}

\[ \text{ZPE} = \sum_i (1/2)\hbar v_i, \]

where $v_i$ 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\textsuperscript{24,26}

\[ \epsilon_d^p = \frac{\int_{E_F}^{E_{dM}} \rho_d(E) dE}{\int_{E_F}^{E_{dM}} \rho_d(E) dE}, \]

where $\rho_d$ 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 ($\epsilon_p^p$) is calculated by the similar way.

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.\textsuperscript{27} Herein, we collect and cite the adsorption energy of most stable adsorption site and the con-
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$_3$NH$_2$, CH$_3$, and NH$_2$ on the top and bridge site of this surface [Fig. 3(b)]. CH$_3$NH$_2$ 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$_3$NH$_2$ 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$_2$ adsors 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...
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 ΔH=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, Ea, is calculated in terms of equation of \( E_a = E_{TS} - E_{TS}/M \), 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 an 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, CH₂NH₂ 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 II. Properties of the TSs of C–N cleavage of CH₃NH₂ on the clean, C(N, O)-modified Mo(100), Mo₂C(100), MoN(100), and Pt(100) surfaces (unit in angstrom).

<table>
<thead>
<tr>
<th>Metal surface</th>
<th>( R_{C,N} )</th>
<th>( R_{X,Mo} )</th>
<th>Site</th>
<th>( R_{X,Mo} )</th>
<th>Site</th>
<th>( R_{X,Mo} )</th>
<th>Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(100)</td>
<td>2.30</td>
<td></td>
<td></td>
<td>3.00</td>
<td>Top</td>
<td>2.05</td>
<td>Top</td>
</tr>
<tr>
<td>Mo(100)–C</td>
<td>2.57</td>
<td>0.44</td>
<td>4h</td>
<td>3.21</td>
<td>Top</td>
<td>1.99</td>
<td>Top</td>
</tr>
<tr>
<td>Mo(100)–N</td>
<td>2.41</td>
<td>0.43</td>
<td>4h</td>
<td>2.85</td>
<td>Top</td>
<td>2.02</td>
<td>Top</td>
</tr>
<tr>
<td>Mo(100)–O</td>
<td>2.49</td>
<td>0.59</td>
<td>4h</td>
<td>2.95</td>
<td>Bridge</td>
<td>2.02</td>
<td>Top</td>
</tr>
<tr>
<td>Mo(100)–p(3×2)–C</td>
<td>2.36</td>
<td>0.58</td>
<td>4h</td>
<td>3.14</td>
<td>Bridge</td>
<td>2.04</td>
<td>Top</td>
</tr>
<tr>
<td>Mo(100)–C(oh)</td>
<td>1.96</td>
<td></td>
<td></td>
<td>2.15</td>
<td>Top</td>
<td>2.41</td>
<td>Top</td>
</tr>
<tr>
<td>Mo(100)–C(oh)</td>
<td>1.91</td>
<td>0.40</td>
<td>4h</td>
<td>2.17</td>
<td>Top</td>
<td>2.31</td>
<td>Top</td>
</tr>
<tr>
<td>Mo₂C(100)</td>
<td>1.95</td>
<td></td>
<td></td>
<td>2.69</td>
<td>Top</td>
<td>2.20</td>
<td>hcp</td>
</tr>
<tr>
<td>MoN(100)</td>
<td>2.06</td>
<td></td>
<td></td>
<td>2.81</td>
<td>Top</td>
<td>2.15</td>
<td>Bridge</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>2.13</td>
<td></td>
<td></td>
<td>2.23</td>
<td>Top</td>
<td>1.99</td>
<td>Top</td>
</tr>
</tbody>
</table>

\( R_{C,N} \) represents the distance between CH₃ and NH₂.
\( X \) represents the preadsorbed surface atom, CH₃, and NH₂, respectively.
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 CH3NH2, and the activity difference 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(Ef), are 2.58, 2.09, 2.30, and 2.27 states/eV/atom after the CH3NH2 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 CH3NH2. Before the adsorption of CH3NH2, 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 CH3NH2, the 2p-band center of the modifiers for the C(N,O)-modified surfaces, −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
modification of atom are resulted from a common reason, i.e., the competition in the adsorptions of C(N,O) and CH₂NH₂.

High-resolution electron energy loss spectroscopy experiments 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.

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.” 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), 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.

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. 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 489.61 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 (θ=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. In addition, the on-surface adsorbed atoms behave entirely different from the corresponding subsurface inserted atoms. Chen et al. have 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. 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 568.71 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...
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 has 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 coeffect 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, CH$_3$NH$_2$ has been dissociated into CH$_3$ and NH$_2$, 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$_{(suf)}$] [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 Mo$_2$C(100) and MoN(100) surfaces

In this section, we take the activation of C–N bond in CH$_3$NH$_2$ on the Mo$_2$C(100) and MoN(100) surfaces as an example to study the reaction on the real catalysts. On the Mo$_2$C(100) surface, the C–N cleavage starts with the elongate of the C–N bond in CH$_3$NH$_2$ adsorbed on the top site, and completes with the two different location of CH$_3$ and NH$_2$. In the two FSs, the NH$_2$ both sits on the hcp site, whereas the CH$_3$ 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 CH$_3$ and NH$_2$ both locating on the hcp site in the FS as an example to describe the C–N bond breaking on the Mo$_2$C(100). The calculated activation energy without the ZPE correction is 2.11 eV. In the TS, the methylamine has dissociated into CH$_3$ and NH$_2$. CH$_3$ and NH$_2$ 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 CH$_3$ prefers the off-top site and the NH$_2$ is on the bridge site about 3 Å away. In the TS, the dissociated CH$_3$ and NH$_2$ are adsorbed on the top site and the
neighboring bridge site with the C–N length of 2.06 Å. There is an imaginary frequency of 614.61 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 Mo$_2$C(100) (2.11 eV) and MoN(100) (2.37 eV) surfaces are clearly increased. This indicates that the reactivities of Mo$_2$C(100) and MoN(100) are lower than the Mo(100), which can be attributed to the downshift of 6-band center $[-1.77$, $-3.05$, and $-3.43$ eV for Mo(100), Mo$_2$C(100), and MoN(100), respectively].

For Mo$_2$C(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 Mo$_2$C(100) surface, the distance between two metallic Mo atoms on the top layer is only $\sim 3.0$ 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 $\sim 3.15$–$3.20$ Å). This may reduce the activity of Mo atom. More importantly, the d-band center of metallic Mo on Mo$_2$C(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 methylene 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 CH$_3$NH$_2$. 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 Mo$_2$C(100), and it is similar to the result of 2.37 eV on the MoN(100). In the TS, the methylene has dissociated into CH$_3$ and NH$_2$. Both CH$_3$ and NH$_2$ are adsorbed on the neighboring top sites with the distance of 2.13 Å. There is an imaginary frequency of 612.3 cm$^{-1}$ corresponding to the C–N stretching vibration. The reaction is exothermic by 0.15 eV.

7. Barrier decomposition

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

$$E_a = \Delta E_{\text{sub}} + \Delta E_{\text{def}} - E_{\text{CH}_3\text{NH}_2} - E_{\text{CH}_3} + E_{\text{NH}_2},$$

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

We collected the contributions to the activation energy of each term in Table IV. From the results, we can see that $\Delta E_{\text{sub}}$ 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$_{\text{sub}}$–C$_{\text{sub}}$ surface, which indicates a slight increase in the energy barrier. The $\Delta E_{\text{def}}$ can be characterized by the distance between carbon and nitrogen ($R_{\text{C–N}}$) of the CH$_3$NH$_2$ in TS (Table III and Fig. 1). From Fig. 1, it is clear that the $R_{\text{C–N}}$ increases with the order of

Mo(100) (2.30 Å) < Mo(100)–p(3×2)–C (2.36 Å) < Mo(100)–N (2.41 Å) < Mo(100)–O (2.49 Å) < Mo(100)–C (2.57 Å)

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

<table>
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<th>$\Delta E_{\text{sub}}$ ($\text{eV}$)</th>
<th>$\Delta E_{\text{def}}$ ($\text{eV}$)</th>
<th>$E_{\text{IS}}$ ($\text{eV}$)</th>
<th>$E_{\text{TS} +}$ ($\text{eV}$)</th>
<th>$E_{\text{TS} -}$ ($\text{eV}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(100)</td>
<td>0.13</td>
<td>2.86</td>
<td>1.04</td>
<td>-4.16</td>
<td>-0.90</td>
</tr>
<tr>
<td>Mo(100)–C</td>
<td>0.18 (0.05)</td>
<td>3.53 (0.67)</td>
<td>1.06 (0.02)</td>
<td>-3.53 (0.63)</td>
<td>-0.34 (0.56)</td>
</tr>
<tr>
<td>Mo(100)–N</td>
<td>0.22 (0.09)</td>
<td>3.23 (0.37)</td>
<td>1.05 (0.01)</td>
<td>-4.08 (0.08)</td>
<td>-0.87 (0.03)</td>
</tr>
<tr>
<td>Mo(100)–O</td>
<td>0.20 (0.07)</td>
<td>3.24 (0.38)</td>
<td>1.01 (0.03)</td>
<td>-4.17 (0.01)</td>
<td>-0.80 (0.11)</td>
</tr>
<tr>
<td>Mo(100)–p(3×2)–C</td>
<td>0.09 (0.04)</td>
<td>2.95 (0.09)</td>
<td>1.10 (0.06)</td>
<td>-3.99 (0.17)</td>
<td>-0.61 (0.29)</td>
</tr>
<tr>
<td>Mo(100)–C$_{\text{sub}}$</td>
<td>0.02 (0.11)</td>
<td>1.63 (1.23)</td>
<td>1.17 (0.13)</td>
<td>-5.95 (1.79)</td>
<td>-2.05 (1.15)</td>
</tr>
<tr>
<td>Mo(100)–C$<em>{\text{sub}}$–C$</em>{\text{sub}}$</td>
<td>0.25 (0.12)</td>
<td>2.27 (0.59)</td>
<td>0.93 (0.11)</td>
<td>-5.49 (1.33)</td>
<td>-2.35 (1.45)</td>
</tr>
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</table>
In summary, this work represents a systematic theoretical study on the methylene 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 electronagative 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 methylene 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) surfaces are lower compared to Mo(100). This work provides a systematic understanding of the catalytic activity of the early transition metal catalysts, which is important for the design and development of new catalysts.
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 CH3NH2 in this work, and do not consider other possible steps including the C–N bond broken. For example, Johnson et al.31 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-η2-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.

ACKNOWLEDGMENTS

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