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Abstract: To predict where a catalytic reaction should occur is a fundamental issue scientifically. Technologically, it is also important because it can facilitate the catalyst’s design. However, to date, the understanding of this issue is rather limited. In this work, two types of reactions, CH₄ ↔ CH₃ + H and CO ↔ C + O on two transition metal surfaces, were chosen as model systems aiming to address in general where a catalytic reaction should occur. The dissociations of CH₄ ↔ CH₃ + H and CO ↔ C + O and their reverse reactions on flat, stepped, and kinked Rh and Pd surfaces were studied in detail. We find the following: First, for the CH₄ ↔ CH₃ + H reaction, the dissociation barrier is reduced by ~0.3 eV on steps and kinks as compared to that on flat surfaces. On the other hand, there is essentially no difference in barrier for the association reaction of CH₃ + H on the flat surfaces and the defects. Second, for the CO ↔ C + O reaction, the dissociation barrier decreases dramatically (more than 0.8 eV on Rh and Pd) on steps and kinks as compared to that on flat surfaces. In contrast to the CH₃ + H reaction, the C + O association reaction also preferentially occurs on steps and kinks. We also present a detailed analysis of the reaction barriers in which each barrier is decomposed quantitatively into a local electronic effect and a geometrical effect. Our DFT calculations show that surface defects such as steps and kinks can largely facilitate bond breaking, while whether the surface defects could promote bond formation depends on the individual reaction as well as the particular metal. The physical origin of these trends is identified and discussed. On the basis of our results, we arrive at some simple rules with respect to where a reaction should occur: (i) defects such as steps are always favored for dissociation reactions as compared to flat surfaces; and (ii) the reaction site of the association reactions is largely related to the magnitude of the bonding competition effect, which is determined by the reactant and metal valency. Reactions with high valency reactants are more likely to occur on defects (more structure-sensitive), as compared to reactions with low valency reactants. Moreover, the reactions on late transition metals are more likely to proceed on defects than those on the early transition metals.

1. Introduction

To predict where a catalytic reaction occurs, whether the reaction happens on flat surfaces or defects (such as steps and kinks), is very important as well as enormously challenging because of the following two reasons: Scientifically, it is one of the most fundamental issues in chemistry. Technologically, it has long been believed that the catalyst design would be tremendously aided once the reaction site is known. It has been observed that for some reactions the reaction rate changes dramatically with the catalyst structure; for example, the reaction rate increases significantly from single-crystal surfaces to small particles in which there are a large number of defects, while for other reactions, the reaction rate is independent of the catalyst structure. Qualitatively, two classes of catalytic processes have therefore been named: the structure-sensitive and structure-insensitive reactions.1 With the aim to design the best catalyst, the surface structure effect on reactions has been extensively studied over the past 40 years.1–24 To date, many observations have been reported. However, the understanding of the surface
structure effect is rather limited. This is largely due to the difficulty to measure microscopic reaction pathways experimentally. In this paper, we report a detailed density functional theory (DFT) study on two fundamental processes, that is, C–H bond and C–O bond cleavage/formation, on flat, stepped, and kinked transition metal surfaces (Rh and Pd). With a careful examination of the calculated results, we have obtained an insight into where a catalytic reaction would occur on metal surfaces.

It has been long observed that the bond breaking processes in hydrocarbon conversion reactions are generally aided by corrugated surfaces; these reactions are structure-sensitive. In particular, kinks appear to be the most active sites for breaking any of the chemical bonds that are available during the hydrocarbon conversion reactions. Taking the hydrogenolysis reaction that requires C–C bond scission as an example, we find that its reaction rate increases considerably (3- to 5-fold) when kinks are present in high concentrations on Pt surfaces. The structure effect on methane decomposition (CH₂ → CH₃ + H) was studied in detail by many surface science techniques. On Ni, Beebe et al. observed that Ni(110) is the best for CH₄ dissociation among Ni(111), Ni(100), and Ni(110). On Pd, Klier and co-workers reported that Pd(679), the surface with kinks, is the most active one; the reaction rate spans an order of magnitude in the order of Pd(111) < Pd(311) < Pd(679). A summary of the surface structure effect on hydrocarbon conversion reactions can be found in the review article of Somorjai.

Ammonia synthesis (N₂ + H₂ → NH₃) on Fe, Ru-based catalysts was long observed to be very sensitive to the surface structure. Using STM and DFT calculations, Dahl et al. found that the N=N bond breaking on Ru(0001) is at least 9 orders of magnitude slower than that on steps. The reaction barrier on steps was calculated to be ~1.5 eV lower than that on flat surfaces. The same was also found for NO dissociation on Ru(0001). For N₂ and NO dissociation, DFT calculations showed that the transition state (TS) on monatomic steps involves five metal atoms, which is energetically more stable than the four-atom TS on close-packed surfaces. Hammer suggested that the upshift of the d band on steps, that is, an electronic effect which helps to stabilize adsorbates, is the main reason for the barrier reduction in NO dissociation. However, Dahl et al. interpreted the large barrier reduction of N₂ dissociation on steps being mainly due to a geometrical effect on steps.

In contrast to the above structure-sensitive reactions, other reactions are quite inert to the change of surface structure, such as ethylene hydrogenation (CH₂CH₂ + H → CH₃CH₃) on metals. The reaction barriers for ethylene hydrogenation on a series of Pt surfaces are similar, about 0.42 eV. Erlt and Koch concluded that no crystal-plane specificity exists for steady-state CO oxidation on Pd at a temperature range of 300–900 K under low pressures. Recently, a surface science study by Uetsuka et al. showed that the reaction rate of CO oxidation on Pd-steps (Pd(335)) is slightly faster (about 1.5 times) than that on (111) terraces. They found that CO oxidation switches from steps to terraces when the CO coverage is varied. In line with this, DFT calculations of Zhang and Hu showed that for CO oxidation on Pd(111), the reaction barrier is strongly affected by the CO coverage, and the reaction is structure-insensitive at medium CO coverage. On Pt(111), the CO coverage dependency for CO oxidation was also found.

To date, no general framework has been established to understand the surface structure effect, and many puzzles regarding the reactivity of different sites for different reactions have not been rationalized. In particular, the following question remains to be answered: Where is the favored site for a particular reaction? This question can be rephrased as follows:

(i) What kind of reaction may be structure-sensitive and why?

(ii) Is the structure-sensitivity metal-dependent? If it is, what is the reason? To answer these questions, in this work we have chosen two elementary reactions, CH₄ ↔ CH₃ + H and CO ↔ C + O, on two transition metal surfaces (Rh and Pd) as probes to tackle the surface structure effect. For each reaction, different reaction sites, that is, flat (111) face, stepped, and kinked Rh and Pd surfaces were studied. These model systems were selected on the basis of two reasons. Technologically, they are elementary steps in many important processes, such as methane activation and Fischer–Tropsch reactions. Scientifically, they are relatively simple and can thus be considered as prototypical reactions in heterogeneous catalysis. In addition, it should be mentioned that the flat (111) surface (of fcc metal) is close-packed and thus the dominant face in real catalysts, and steps and kinks are perhaps the most common defects.

Our DFT calculations show that surface defects, especially the steps, are generally favored for bond-breaking reactions, while the association reaction (bond making) can be either structure-sensitive or insensitive, depending on individual reactions as well as the particular metal. Physical origins of these trends are identified and discussed. Although only two types of reactions on Rh and Pd were tackled in this study, the understanding we have obtained is of general chemical interest. This paper is organized as follows: The calculation methods are described in section 2. In section 3, calculation results, that is, the reaction pathways and energetics for CH₄ → CH₃ + H and CO ↔ C + O on flat surfaces, steps, and kinks, are reported. Their transition state geometries are compared and discussed. In section 4, we discuss the origin of the surface structure effect on these reactions. In the last section, conclusions are summarized.

2. Calculation Methods

Density functional theory calculations with the generalized gradient approximation were performed. The electronic wave functions were expanded in a plane wave basis set, and the ionic cores were described by ultrasoft pseudopotentials. The vacuum region between slabs was
10 Å, and a cutoff energy of 340 eV was used. Monkhorst-Pack k-point sampling with 0.07 Å⁻¹ spacing was utilized for all of the calculations (for example, for a p(2×2) Rh(111) slab, 3×3×1 k-point sampling is used).

To fully compare the reactivity of flat and corrugated surfaces for a reaction, we have modeled the flat surfaces, Rh(111) and Pd(111), using large unit cells that correspond to the low coverage of reactions. The CH₄ ↔ CH₃ + H reactions were preformed in the p(2×5) unit cell (1/6 monolayer (ML)) with four layers, and the CO ↔ C + O reactions were in the p(3×3) unit cell (1/6 ML) with three layers. We found that for CH₄ ↔ CH₃ + H reactions, the coverage effect on the dissociation barriers is very small (below 0.1 eV), and for CO ↔ C + O reactions, the coverage effect is about 0.1 eV. All of the flat surfaces were fixed at the bulk-truncated structures because the surface relaxations of Rh(111) and Pd(111) have a very small effect on the reaction barriers (below 0.1 eV) when the large unit cells are used. We have checked the barrier of CH₄ dissociation on a series of Rh(111) slabs in detail; see ref 28. The zero point energy is not included.

The Rh-step and the Pd-step were modeled by (1×2) unit cells (1/6 ML) of Rh(211) and Pd(211), respectively (see Figure 1a). The (211) surface contains steps of (100)-type, which is found to be more active than the (111)-type step in catalytic reactions. The kinked surfaces were constructed by removing one edge atom at the step in a (1×3) unit cell of the (211) surface (see Figure 1b). Hereafter, the kinked surfaces obtained from Rh(211) and Pd(211) are named as the Rh-kink and the Pd-kink, respectively. All of the corrugated surfaces were modeled with “effective” three layers (see Figure 1a, side view) with the top layer being relaxed and the other layers being fixed at the bulk-truncated structure. It should be mentioned that the least coordination number (CN) of metal atoms on these surfaces is different: It reduces from the flat surfaces to the steps and to the kinks, for example, on Rh(111) the CN = 9, on Rh-steps CN = 7 (the metal atom of the EB site, Figure 1a), and on Rh-kinks CN = 6 (the metal atom of the KB site, Figure 1b). TSs of reactions were searched using a constrained minimization technique. The TS was identified when (i) the force on the atoms vanish and (ii) the energy is a maximum along the reaction coordinate, but a minimum with respect to all of the remaining degrees of freedom. Our previous work has demonstrated that the above DFT setup affords a good accuracy, especially for the calculation of reaction barriers in heterogeneous catalysis.

3. Results and Discussions

3.1. CH₄ ↔ CH₃ + H on Flat and Corrugated Surfaces

Being the essential step for methane conversion, CH₄ → CH₃ + H on metals has been a hot subject focused by many experimental and theoretical studies over the last several decades. The general consensus obtained from experiments can be summarized as follows: (i) Over transition metal surfaces, CH₄ dissociation occurs at relatively low temperatures, even on Pd (400 K); (ii) the process is assisted by the vibrational energy of methane; and (iii) the apparent activation energies are low, but the reactive sticking probabilities are also low. On several close-packed metal surfaces, such as Ni(111), Ru(0001), and Pd(111), the apparent CH₄ dissociation barriers (Eₐₑff) have been measured experimentally. On Ni(111), Eₐₑff is about 0.55 eV, reported by Beebe et al. and Ceyer et al.; on Ru(0001), Eₐₑff is 0.37 eV by Wu et al., by Klier et al. As mentioned in the Introduction, CH₄ dissociation was found to be structure-sensitive. On corrugated surfaces, it is generally higher than that on flat surfaces. Theoretically, CH₄ dissociation on Ni(111) and Ru(0001) has been calculated using DFT. Two groups have reported similar barriers for CH₄ dissociation on Ni(111), ~0.8 eV, while the others reported even higher barriers. Ciobica et al. obtained a barrier of 0.88 eV for methane dissociation on Ru(0001), and it was calculated to be 0.79 eV by us.

When comparing the experimental values to the DFT barriers, it is quite surprising to find that the barriers obtained from DFT calculations are generally several tenths of an eV (0.3–0.4 eV) larger than the measured barriers. The reason for this inconsistency is unknown yet. Two possibilities might be involved: (i) In real systems, CH₄ dissociation may not occur on the flat
Winters, might exist, which largely reduces the effective barrier (ii) A quantum-mechanical tunneling mechanism, suggested by the chemisorption energies (sensitivity of methane dissociation, we have investigated CH4 elucidate the above puzzle and shed light on the structure-
possibility (i) therefore could not be ruled out. With the aim to
Other DFT studies showed that on Ni(111), 40 Cu(111), 41 and
Pd surfaces.

Table 1. The CH3 and H Atom Adsorption Energies (Ead) and the Adsorption Sites on Different Rh and Pd Surfaces (the Final State for CH4 Dissociation)\(^4\)

<table>
<thead>
<tr>
<th></th>
<th>CH3</th>
<th>H</th>
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<tbody>
<tr>
<td></td>
<td>Ead</td>
<td>site</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>1.88</td>
<td>fcc 2.262</td>
</tr>
<tr>
<td>Rh-step</td>
<td>2.16</td>
<td>EB 2.078, 2.344</td>
</tr>
<tr>
<td>Rh-kink</td>
<td>2.16</td>
<td>KB 2.100, 2.362</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>1.78</td>
<td>top 2.058</td>
</tr>
<tr>
<td>Pd-step</td>
<td>2.01</td>
<td>EB 2.117, 2.278</td>
</tr>
<tr>
<td>Pd-kink</td>
<td>1.88</td>
<td>KB 2.195, 2.182</td>
</tr>
</tbody>
</table>

\(^4\) The structures of the step and the kink and chemisorption sites (EB, KB) are shown in Figure 1. The distances for the CH3 to its nearest-neighboring metal atoms (d(C-metal)) are also listed. For the H atom, its adsorption energies on flat surfaces, steps, and kinks are very similar (within 0.05 eV), and thus the Ead on the flat surfaces is used for all of the surfaces.

Figure 2. The top view of the calculated TS structures for CH3 ↔ CH3 + H reactions on Rh(111) (a), Rh-step (b), and Rh-kink (c). Side views of the TSs on the Rh(111) and the Rh-step are shown in insets in (a) and (b), respectively. The TSs for CH3 ↔ CH3 + H on Pd surfaces are similar. The small gray balls, small yellow balls, and big balls are C atoms, H atoms, and Rh atoms, respectively. In particular, the step-edge Rh atoms in the Rh-step and the Rh-kink are shown as big white balls.

Table 2. The Important Structural Parameters (Distances, \(d\), Angle, \(\angle\)) for the TSs of CH4 ↔ CH3 + H on Different Rh and Pd Surfaces\(^4\)

<table>
<thead>
<tr>
<th></th>
<th>CH3 ↔ CH3 + H</th>
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<tbody>
<tr>
<td></td>
<td>d(C-metal) (Å)</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>2.206</td>
</tr>
<tr>
<td>Rh-step</td>
<td>2.168</td>
</tr>
<tr>
<td>Rh-kink</td>
<td>2.140</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>2.157</td>
</tr>
<tr>
<td>Pd-step</td>
<td>2.155</td>
</tr>
<tr>
<td>Pd-kink</td>
<td>2.120</td>
</tr>
</tbody>
</table>

\(^4\) The TSs are shown in Figure 2. H3 is the reacting H atom in CH3 ↔ CH3 + H.

Ru(0001),\(^38\) CH3 sits on the hollow site, while on 5d metal, for example, Pt(111),\(^41\) it is on the top site.

On all of the corrugated surfaces, that is, steps and kinks, the most stable chemisorption site for CH3 is always the bridge site of the step-edge (EB site or KB site in Figure 1). Generally, the steps improve the CH3 chemisorption energy by several tenths of an eV as compared to the flat surfaces, while there is no further energy gain when the CH3 shifts from the steps to the kinks. For example, Ead(CH3) = 2.16 eV on both Rh-step and Rh-kink, and this value is 0.28 eV higher than that on Rh(111). It is interesting to note that the H atom adsorption is insensitive to the surface change: The difference between the calculated Ead(H) on the steps and kinks and that on the flat surfaces is less than 0.05 eV. Thus, we take the H atom at the flat surfaces as the final state (FS) of the H atom after CH4 dissociation.

3.1.2. Reaction Pathways and Barriers of CH4 ↔ CH3 + H. On flat Rh(111) and Pd(111), CH3 dissociation occurs over a top site of a metal atom. Figure 2a shows the located TS geometry on Rh(111) (the TS on Pd(111) is similar). At the TS, the CH3 sits on the top site, and the activated H atom is near a fcc hollow site. The important TS structural parameters are listed in Table 2. This TS structure is similar to previous results for CH3 dissociation on other close packed surfaces, for example, Ni(111), Pt(111), and Ru(0001). Here we summarize two general features of the TS of methane dissociation on these surfaces. First, the TSs belong to “late TSs” (close to the final state). This is evident from the located TS structures: (i) The H—CH3 bonds at the TSs are well stretched as compared to the C—H bond length of methane (1.5—1.6 Å at the TSs (Table 2) and 1.08 Å in the CH4 molecule). (ii) The metal—CH3 and metal—H bond distances are rather short and close to the geometries on Rh(111) and Pd(111), the CH3 is the most stable at the fcc hollow site (Rh(111), Ead(H) = 2.92 eV; Pd(111), Ead(H) = 3.05 eV). The potential energy surface of CH3 is quite flat on both metals; CH3 slightly prefers the fcc hollow site on Rh(111) (Ead(CH3) = 1.88 eV, 0.12 eV more stable than that on a top site); it preferably sits on the top site on Pd(111) (Ead(CH3) = 1.78 eV, 0.08 eV more stable than that on a fcc hollow site), which is consistent with the previous calculation of Paul and Sautet.\(^39\) Other DFT studies showed that on Ni(111),\(^40\) Cu(111),\(^41\) and


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optimized distances of the individual CH₃ and H adsorption, respectively. For example, the optimized Rh−CH₃ bond length (CH₃ sitting at a top site) is 2.107 Å, while the Rh−CH₃ distance at the TS is 2.206 Å (Table 2). It should be mentioned that the late TS of methane dissociation is consistent with the experiment that CH₄ dissociation is assisted by vibrational energies. Second, each TS mainly involves one metal atom, on which the CH₃ sits. The H atom, although near the fcc hollow site, does not bond with the other two surface atoms strongly, as is evident from the distances of the H atom to the three metal atoms at the TS (Table 2).

We then located the most stable TSs for CH₄ dissociation on steps, the Rh-step and the Pd-step (see Figure 1a) and kinks, the Rh-kink and the Pd-kink (shown in Figure 1b, see Calculation Methods). Figure 2b and c shows the TSs for CH₄ dissociation on the Rh-step and the Rh-kink (the TSs on the Pd-step and the Pd-kink are similar to the Rh counterparts). As can be seen from Figure 2b and c, the TSs on the steps and the kinks in fact are very similar: Both locate at the step-edge, in which CH₃ sits on the top site of one edge metal atom, and the H atom is near the bridge site of the step-edge. The important TS structural parameters on the steps and the kinks are listed in Table 2, together with those on the flat surfaces. With a careful comparison, we found that the TSs on the steps and the kinks share the same basic features with the TS on the flat surfaces (Figure 2a). The TSs on the steps and the kinks also (i) belong to late TSs and (ii) mainly involve one metal atom. In fact, the TSs on the steps and the kinks may be even “later”. For instance, at the TS on the Pd-step, d(CH₃−CH₃) is 1.595 Å; on the Pd-kink, it is 1.691 Å, as compared to 1.540 Å on Pd(111).

With all of the states being determined, we then calculated the dissociation barrier (Eₐ dis) for CH₄ ↔ CH₃ + H as well as the association barrier (Eₐ as) for the reverse reaction, CH₃ + H → CH₄. Figure 3 illustrates in general all of the energy terms used in Table 3 for a dissociation reaction and the reverse reaction. Eₐ as is 0.59 eV on Rh(111) and 0.62 eV on Pd(111). It is noticed that the reaction energies (∆H) the energy difference between the initial state (IS) and the FS, ∆H = Eₐ as − Eₐ dis, see Figure 3) are almost zero for CH₄ ↔ CH₃ + H on Rh(111) and Pd(111). On the steps and the kinks, we found that the Eₐ dis decreases considerably: Eₐ dis = 0.32 eV on the Rh-step and 0.20 eV on the Rh-kink; Eₐ dis = 0.38 eV on the Pd-step and 0.41 eV on the Pd-kink. However, Eₐ as of the CH₃ + H reaction on the steps is similar to that on the flat surfaces, and they only decrease by ~0.1 eV if the reaction occurs on the kinks (Table 3).

### 3.1.3. Discussion of the Reaction Mechanism of CH₄ ↔ CH₃ + H on Transition Metals

As mentioned before, for CH₄ dissociation on close-packed surfaces, for example, Ni(111) and Ru(0001), the barriers calculated from DFT are about 0.3 eV larger than the values measured experimentally. This is also true on Pd(111), as we compared our calculated barrier for CH₄ dissociation on Pd(111) (0.67 eV) to the value recently reported by Klier et al. (0.36 eV (34.3 kJ/mol)). However, we found interestingly that for the barriers on the steps and the kinks, the consistency between our results and the experimental ones reported by Klier et al. is very good. The effective barriers for methane dissociation on Pd(311) (with steps) and Pd(679) (with kinks) are 0.33 eV (32.2 kJ/mol) and 0.44 eV (43.9 kJ/mol), respectively, and our calculated ones are 0.38 eV on Pd-steps and 0.41 eV on Pd-kinks. In addition, our barriers on the step and the kink of Rh (0.2−0.3 eV) are in good agreement with the early experiment work of Ehrlich et al., who reported the barrier of methane dissociation on Rh films being ~0.3 eV.

To reconcile the above puzzle, we have done the following analysis on the reaction rate. Using the Arrhenius equation, we estimated the initial sticking coefficients (S₀) as

\[ S₀ \approx A \exp(-E_a/RT)[\text{sites}] \]

where T is assumed to be 500 K, A is the preexponential factor, and [sites] is the concentration of reaction sites. A small change in Eₐ will lead to a large change in reaction rate (S₀); a 0.3 eV change in Eₐ (e.g., CH₄ dissociation goes from flat surfaces to steps) will lead to S₀ differing by 10³ if everything else is the same. Even assuming the population of the stepped sites is only 1% of the flat surface sites and A is constant, we find that the S₀ on steps (S₀ step) is still ~10 times larger than S₀ on flat surfaces (S₀ flat). Therefore, the overall S₀ is dominated by S₀ step, and the effective barrier E eff would be largely determined by Eₐ dis on steps. This means that the measured Eₐ eff would correspond to Eₐ dis on steps, which is ~0.3 eV smaller than the Eₐ dis on flat surfaces. Therefore, this indicates that the CH₄ dissociation reaction should be structure-sensitive (Table 2). On the other hand, a barrier decrease of 0.1−0.2 eV can only increase exp(−E_a/RT) by 10−100 times at 500 K, which is likely to be tempered by the number of the active sites. This suggests that the CH₃ + H association is largely structure-insensitive because its barrier (Eₐ as) variation is small (Table 2).

| Table 3. The Calculated Dissociation Barriers (Eₐ dis) for CH₄ ↔ CH₃ + H and CO → C + O and the Barriers (Eₐ as) for Their Reverse Reactions on Different Rh and Pd Surfaces |
|----------------|----------------|----------------|----------------|----------------|----------------|
|                | Rh(111)        | Rh-step        | Rh-kink        | Pd(111)        | Pd-step        |
| CH₄ ↔ CH₃ + H  | 0.67           | 0.59           | 0.20           | 0.66           | 0.38           |
| CO ↔ C + O     | 1.17           | 0.49           | 0.21           | 1.87           | 0.63           |
| CN             | 9              | 7              | 6              | 9              | 7              |

* The least coordination number (CN) of the metal atoms involved in the TSs on flat surfaces, steps, and kinks are listed for comparison. The unit of the barriers is eV.
On the basis of these results, we suggest that \( \text{CH}_4 \) dissociation even on single crystal surfaces may be dominated by a small number of defects, especially steps, considering that steps always exist on single crystal surfaces. Kinks may not play an important role due to their much smaller population than steps and the similar reactivity with steps. This suggestion can be used to reconcile the puzzle mentioned before. The experimentally measured barrier for \( \text{CH}_4 \) dissociation on Pd(111) is lower (0.3 eV) than the calculated one on the flat surface, but is very close to that calculated on the steps and the kinks. Moreover, the population of stepped sites on a surface is expected to be the controlling factor to the reaction rate. This is indeed what was observed experimentally. Klier et al. found that \( \text{CH}_4 \) dissociation on Pd(679) is about 10 times faster than that on Pd(111), the magnitude of which is consistent with the difference of the step population between two surfaces: 13% of Pd(679) are steps, while there are at least 1% steps on Pd(111). It should be mentioned that on the basis of our calculations, we believe that the tunneling effect in \( \text{CH}_4 \) dissociation might not be very crucial, which was also suggested in a recent paper.\(^{15}\)

It is worth mentioning some nice experiment work of Egeberg et al.,\(^{16}\) which was just published very recently. Egeberg et al. carefully studied the dissociation of \( \text{CH}_4 \) on Ni(111) and Ru(0001) to examine whether the stepped sites have a large effect on \( \text{CH}_4 \) dissociation. They reported that sputtering of the Ni(111) surface without subsequent annealing was found to increase the initial sticking by 2\(^{11}\) at 16 eV\(^{11}\). This can be readily explained by our DFT calculations: The TS of \( \text{CH}_4 \) dissociation only involves one metal atom (even on steps), which is different from the TS of \( \text{N}_2 \) dissociation (involving the five-atom on steps). Therefore, the Au deposition could not block the dissociation site of \( \text{CH}_4 \) dissociation on steps (may have some electronic effect, see discussion in section 4), but completely blocks that of \( \text{N}_2 \) dissociation (also see section 4).

As mentioned before, our calculation results show that the reverse reaction of \( \text{CH}_4 \) dissociation, \( \text{CH}_3 + \text{H} \rightarrow \text{CH}_2 \), is quite inert to the structure change. One piece of evidence to support the C–H bond formation being structure-insensitive is that the ethylene hydrogenation (\( \text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3=\text{CH}_3 \)) reactions on Pt and Rh were found to be structure-insensitive.

### 3.2. \( \text{CO} \leftrightarrow \text{C} + \text{O} \) on Flat and Corrugated Surfaces

Using syngas (\( \text{CO} + \text{H}_2 \)) to produce hydrocarbons is one of the most important industrial processes in heterogeneous catalysis. \( \text{CO} \) dissociation (\( \text{CO} \rightarrow \text{C} + \text{O} \)), which produces the active surface carbons, appears to be an essential step for \( \text{CH}_4 \) formation (\( \text{CO} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2 \)).

As mentioned before, our calculation results show that the reverse reaction of \( \text{CH}_4 \) dissociation, \( \text{CH}_3 + \text{H} \rightarrow \text{CH}_2 \), is quite inert to the structure change. One piece of evidence to support the C–H bond formation being structure-insensitive is that the ethylene hydrogenation (\( \text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3=\text{CH}_3 \)) reactions on Pt and Rh were found to be structure-insensitive.

### 3.2.1. Reaction Pathways and Barriers of \( \text{CO} \leftrightarrow \text{C} + \text{O} \) on Flat Surfaces

We have calculated \( \text{CO} \leftrightarrow \text{C} + \text{O} \) on a series of flat 4d and 5d close-packed surfaces, that is, Ru(0001), Rh(111), Pd(111), Os(0001), Ir(111), and Pt(111) at \( 1/4 \) ML coverage previously (see ref 30b). We have shown that on these surfaces, the TSs of \( \text{CO} \) dissociation are similar: They are all late TSs. In addition to the previous work, in this work we have recalculated \( \text{CO} \) dissociation at a low coverage on Rh(111) and Pd(111), \( 1/6 \) ML (\( p(3 \times 3) \) unit cell), to better compare the reactivity between different surface structures (the decrease of coverage will change the barriers slightly because the TS and the FS are more stable at low coverages; for example, the \( \text{CO} \) dissociation barrier on Rh(111) at \( 1/6 \) ML is 1.25 eV, and it is 1.17 eV at \( 1/9 \) ML). Figure 4a shows the TS structure for \( \text{CO} \) dissociation on Rh(111) (the TS on Pd(111) is similar). At the TS, the C atom is near the hcp hollow site, and the O atom is close to a bridge site. The important TS structural parameters are listed in Table 4. It appears that at the TS, four surface atoms

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**Figure 4.** The top view of the calculated TS structures for \( \text{CO} \leftrightarrow \text{C} + \text{O} \) reactions on Rh(111) (a), Rh-step (b), and Rh-kink (c). The side view of the TS on the Rh-step is shown in the inset in (b). The TSs for \( \text{CO} \leftrightarrow \text{C} + \text{O} \) on Pd surfaces are similar to those on Rh. The small gray balls, small red balls, and big balls are C atoms, O atoms, and Rh atoms, respectively. In particular, the step-edge Rh atoms in the Rh-step and the Rh-kink are shown as big white balls.
The TSs are shown in Figure 4. In all of the TS structures, the C atom is on the three-fold hollow site, and the O atom is on the bridge site (see Figure 4a–c). The calculated adsorption energies (E_{ad}) at 1/3 ML are as follows: on Rh(111), E_{ad}(C) = 7.12 eV and E_{ad}(O) = 4.78 eV, and on Pd(111), E_{ad}(C) = 6.85 eV and E_{ad}(O) = 4.39 eV. The dissociation barriers (E_{ad}^{dis}) and the association barriers of CO ↔ C + O were calculated and listed in Table 3, together with those of the CH_{4} ↔ CH_{3} + H reaction.

3.2.2. Reaction Pathways and Barriers of CO ↔ C + O on Steps and Kinks. We then investigated CO dissociation on the Rh-step, the Pd-step, the Rh-kink, and the Pd-kink. CO dissociation on these defects possesses very similar TS structures. Figure 4b and c depicts the TS structures on the Rh-step and the Rh-kink, respectively. At the TSs, the O is at the bridge site of a step-edge, and the C atom sits on the fcc site of the terrace near the step. It is obvious that there are five atoms involved in bonding with the TS complex, while it is only four on flat surfaces. The important structural parameters for the TSs are listed in Table 4. These types of TS structures on steps or kinks are similar to N2 and NO dissociation on Ru-steps, as are listed in Table 4. These types of TS structures on steps or flat surfaces. The important structural parameters for the TSs are shown in Table 4. The calculated adsorption energies (E_{ad}) at 1/3 ML are as follows: on Rh(111), E_{ad}(C) = 7.12 eV and E_{ad}(O) = 4.78 eV, and on Pd(111), E_{ad}(C) = 6.85 eV and E_{ad}(O) = 4.39 eV. The dissociation barriers (E_{ad}^{dis}) and the association barriers of CO ↔ C + O were calculated and listed in Table 3, together with those of the CH_{4} ↔ CH_{3} + H reaction.

| Table 4. The Important Structural Parameters (Distances, d) for the TSs of CO ↔ C + O on Different Rh and Pd Surfaces^a |
|-----------------|-----------------|-----------------|
|                 | d_{C-metal} | d_{C-metal} | d_{C-O} |
| Rh(111)         | 1.890, 1.959, 2.029 | 2.046, 2.145 | 1.865 |
| Rh-step         | 1.904, 1.943, 1.943 | 1.966, 1.966 | 2.090 |
| Rh-kink         | 1.911, 1.947, 1.947 | 1.975, 1.975 | 2.090 |
| Pd(111)         | 1.885, 1.935, 2.019 | 2.009, 2.136 | 1.980 |
| Pd-step         | 1.859, 1.897, 1.897 | 1.930, 1.930 | 2.724 |
| Pd-kink         | 1.886, 1.886, 1.901 | 1.931, 1.931 | 2.500 |

^a The TSs are shown in Figure 4. In all of the TS structures, the C atom is on the three-fold hollow site, and the O atom is on the bridge site (see Figure 4a–c).
O reaction can be considered as a process requiring a high coordinated site for its TS geometry, and the CH$_4$ ↔ CH$_3$ + H can be considered as a reaction with a low coordination site. Indeed, CO ↔ C + O is highly structure-sensitive. However, there are some limitations in this simple argument. It is not completely correct to state that the CH$_4$ ↔ CH$_3$ + H is structure-insensitive. In fact, the forward and reverse reactions of CH$_4$ ↔ CH$_3$ + H are quite different with respect to the structure-sensitivity.

It is obvious that the above argument, due to its simplicity, does not provide a comprehensive picture of the structural effect on catalytic reactions. We believe that the following two questions need to be answered to provide a real insight into the structure-sensitivity: (i) Why is the reaction type (a dissociation or association reaction) important to the structure-sensitivity? (ii) What are the individual contributions of the electronic effect (defined as $E_g$) and the geometrical effect (defined as $G$) to the reaction barrier? Without knowing these, it is very difficult to predict whether a reaction is structure-sensitive or not, because there are four possible combinations, that is, ($E_1^+ + G_1^-$), ($E_2^- + G_2^-$), ($E_1^- + G_1^+$), and ($E_2^+ + G_2^+$), where $E_1^+$ ($E_1^-$) means that the electronic effect reduces (increases) the barrier and $G_1^+$ and $G_1^-$ are defined in a similar way.

### 4.2. Barrier Decomposition: A Quantitative Understanding

To answer the above questions, we have utilized the following energy decomposition method (also see our previous work, ref 30a,b) to analyze the reaction barriers. For a general reaction of AB ↔ A + B starting from an AB molecule in the gas phase to the adsorbed A and B on surfaces (A and B represent atoms or fragments), one can write the dissociation barrier, $E_{\text{a, dis}}$, as (Figure 3):

$$ E_{\text{a, dis}} = E_{\text{g, bond}} - E_{\text{TS}} $$

where $E_{\text{g, bond}}$ is the A−B bond energy in the gas phase, and $E_{\text{TS}}$ is the total chemisorption energy of A and B at the TS. Because catalytic reactions on metal surfaces generally belong to the “late TS” reactions, $E_{\text{TS}}$ can be further decomposed into three terms (Figure 3):

$$ E_{\text{TS}} = E_{\text{A, TS}} + E_{\text{B, TS}} - E_{\text{int, TS}} $$

where $E_{\text{A, TS}}$ is the chemisorption energy of A at the TS geometry without B; $E_{\text{B, TS}}$ is defined in a similar way; and $E_{\text{int, TS}}$ is a quantitative measure of the interaction between A and B at the TS. It is usually a positive energy term due to the repulsive nature between A and B at the TS geometry in heterogeneous catalysis. Thus, by combining eqs 1 and 2, we arrive at

$$ E_{\text{a, dis}} = E_{\text{g, bond}} - E_{\text{TS}} = E_{\text{g, bond}} - (E_{\text{A, TS}} + E_{\text{B, TS}}) + E_{\text{int, TS}} $$

Equation 3 suggests that the dissociation barrier ($E_{\text{a, dis}}$) consists of three parts: (i) $E_{\text{g, bond}}$, the bonding energy of AB in the gas phase; (ii) $E_{\text{A, TS}}$ and $E_{\text{B, TS}}$, the individual product (A, B) adsorption energies at the TS; and (iii) $E_{\text{int, TS}}$, the interaction energy between A and B at the TS. In a similar way, the association barrier can be written as the energy difference between the TS and the FS:

$$ E_{\text{a, as}} = E_{\text{FS}} - E_{\text{TS}} = (E_{\text{A, FS}} + E_{\text{B, FS}}) - (E_{\text{A, TS}} + E_{\text{B, TS}}) + E_{\text{int, TS}} $$

Table 5. The Decomposition of the TS Chemisorption Energy ($E_{\text{TS}}$) of CH$_4$ → CH$_3$ + H and CO → C + O on Rh(111) and the Rh-Step (see Figure 3 and Eqs 1–4 for the Meaning of All of the Symbols)\(^a\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CH$_4$ → CH$_3$ + H</th>
<th>CO → C + O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rh(111)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS</td>
<td>$E_{\text{ch}}$</td>
<td>$E_{\text{ch}}$</td>
</tr>
<tr>
<td>FS</td>
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<tr>
<td>Totals</td>
<td>$E_{\text{tot}}$</td>
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<tr>
<td>$E_{\text{FS}}$</td>
<td>$E_{\text{FS}}$</td>
<td>$E_{\text{FS}}$</td>
</tr>
<tr>
<td>$E_{\text{a, as}}$</td>
<td>$E_{\text{a, as}}$</td>
<td>$E_{\text{a, as}}$</td>
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<tr>
<td>$E_{\text{int, TS}}$</td>
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where $E_{\text{a, as}}$ and $E_{\text{a, dis}}$ are the FS and TS chemisorption energies of A and B, respectively. The interaction energy of A and B at the FS, that is, $E_{\text{int, FS}}$, is not included in eq 4. This is because under the reaction condition we studied (low coverages), $E_{\text{int, FS}}$ is normally zero: a large separation between A and B ensures no repulsive interaction between them.

Because all of the TSs we studied are late TSs, $E_{\text{a, TS}}$ and $E_{\text{a, dis}}$ reflect largely the A and B bonding ability on the metal surface. In other words, $E_{\text{a, TS}}$ and $E_{\text{a, dis}}$ are quite close to their FS counterparts, $E_{\text{A, FS}}$ and $E_{\text{B, FS}}$. It is thus expected that $E_{\text{int, TS}}$ and $E_{\text{a, dis}}$ depend, on the one hand, by and large determined by the local electronic effect of metals. The interaction energy, $E_{\text{int, TS}}$, is usually an energy cost due to the repulsive nature between A and B at the late TS. The $E_{\text{int, TS}}$ consists mainly of two parts: (i) the bonding competition, which is caused by A and B sharing bonding with surface atoms; and (ii) the direct Pauli repulsion between A and B. Both are closely related to the TS structure. Thus, $E_{\text{int, TS}}$ is a quantitative measure of the geometrical effect on catalytic reactions.

We used eq 2 to decompose the $E_{\text{TS}}$ of the CH$_4$ ↔ CH$_3$ + H and CO ↔ C + O reactions on Rh(111) and the Rh-step. The individual energy components are listed in Table 5, and the TS chemisorption energies are also listed for comparison. From Table 5, one can see how the surface structure affects the reaction barriers:

(i) For CH$_4$ dissociation, the barrier reduction (about 0.3 eV) from the flat surface to the step is due to the increase of $E_{\text{A, TS}}$, $E_{\text{B, TS}}$, and $E_{\text{int, TS}}$ ($\Sigma E_{\text{TS}}$), which is the local electronic effect ($E_{\text{int, TS}}$'s are almost identical on these two surfaces). For dissociation reactions, the barrier reduction on steps should be generally true because steps always bond adsorbates more strongly ($\Sigma E_{\text{TS}}$ increase) and $E_{\text{int, TS}}$ on steps is not lower than that on flat surfaces (the TS geometry on steps is similar to that on flat surfaces, if not energetically better). For the association reaction of CH$_3$ + H → CH$_4$, although $E_{\text{A, TS}}$ + $E_{\text{B, TS}}$ on the step increases by $\sim$0.3 eV, $E_{\text{A, FS}}$ + $E_{\text{B, FS}}$ also increases by $\sim$0.3 eV as compared to their counterparts on the flat surface. Therefore, $E_{\text{a, as}}$ has almost no change from the flat surface to the step considering that the $E_{\text{int, TS}}$'s are similar on these two surfaces.
(ii) For CO dissociation, $E_{\text{int}}^{\text{TS}} + E_{\text{B}}^{\text{TS}}$ on the step is about 0.23 eV larger than that on the flat surface (the electronic effect), and, remarkably, $E_{\text{int}}^{\text{TS}}$ decreases from 1.11 eV on the flat surfaces to 0.47 eV on steps. In total, $E_{\text{int}}^{\text{TS}}$ on the step is 0.87 eV smaller than that on the flat surface. This large reduction of $E_{\text{int}}^{\text{TS}}$ consists of two components: the electronic effect (0.23 eV) and the geometrical effect (0.64 eV). The geometrical effect is obviously much more important. For the association reaction of $C + O \rightarrow CO$, $E_{\text{int}}^{\text{TS}} + E_{\text{O}}^{\text{TS}}$ on the step is also 0.21 eV larger than that on the flat surface. Thus, the electronic effect stabilizes the TS and the FS in a similar magnitude, the same as that in the CH$_4$ ↔ CH$_3$ + H reaction. Therefore, the reduction of $E_{\text{as}}$ (eq 4) on the step is mainly caused by the large decrease in $E_{\text{int}}^{\text{TS}}$, the geometrical effect.

The barrier-decomposition results can be summarized as follows. First, the local electronic effect stabilizes the TS and the FS in a similar magnitude, which is not surprising, considering that the catalytic reactions on metal usually possess late TS. As a result, it always plays a positive role in reducing the dissociation barrier (eq 3), but little role in reducing the association barrier (eq 4). It should be mentioned that the magnitude of the local electronic effect on the dissociation reaction is found to be small, ~0.3 eV for both CH$_4$ and CO dissociations. Second, the geometrical effect, if it plays a role, can reduce both the dissociation and the association reaction (no role in CH$_4$ ↔ CH$_3$ + H, a significant role in CO ↔ C + O). The magnitude of the geometrical effect can be quite large, for example, 0.64 eV in the CO ↔ C + O reaction.

4.3. Origin and General Trends of the Geometrical Effect. Because the contribution of the geometrical effect on both dissociation and association reactions can be significant, in this subsection we will focus on the origin of this effect and reveal its general trends. As mentioned above, $E_{\text{int}}^{\text{TS}}$ contains mainly two components, that is, the energy cost from the bonding competition effect and the direct Pauli repulsion. The Pauli repulsion is by and large determined by the distance between two reactants. It is noticed that, in CO ↔ C + O on Rh surfaces, because the C–O distances at the TSs on flat Rh(111) (1.87 Å) and the Rh-step (2.09 Å) are not so different (as compared to the 1.13 Å of the CO molecule), the Pauli repulsion contributions to $E_{\text{int}}^{\text{TS}}$ for the reaction on flat Rh(111) and that on the Rh-step should be quite similar. Therefore, the major difference of $E_{\text{int}}^{\text{TS}}$ between the flat Rh(111) and the Rh-step, that is, the geometrical effect, should originate from the variation of the bonding competition effect from the flat surface to the step.

We have done the following analysis on an A + B coadsorption system to quantitatively investigate the magnitude of the bonding competition effect. First, we define a standard bonding competition energy ($E_{\text{int}}^{0}$) for the A + B coadsorption system:

$$E_{\text{int}}^{0} = E_{\text{A}} + E_{\text{B}} - E_{\text{A+B}}$$

where $E_{\text{A+B}}$ is the total chemisorption energy of A + B coadsorption in which A and B are placed at two neighboring hcp sites in a p(2 × 2) unit cell (thus they share surface atoms), with the positions of A and B corresponding to their individual optimized adsorption positions; $E_{\text{A}}$ ($E_{\text{B}}$) is the individual chemisorption energy of A (B). In such a structure, the distance between A and B is about 2.7 Å, at which the direct Pauli repulsion between A and B is believed to be negligible. Thus, $E_{\text{int}}^{0}$ measures mainly the bonding competition effect between A and B. We have calculated $E_{\text{int}}^{0}$ for different atomic pairs, C–C, C–N, C–O, C–H on the 4d metals Ru(0001), Rh(111), and Pd(111). The values are shown in Figure 5. Two general trends can be seen in Figure 5: (i) For each pair, the $E_{\text{int}}^{0}$ increases from the left to the right in the periodical table, Pd > Rh > Ru. (ii) As the adsorbate valency decreases, the $E_{\text{int}}^{0}$ decreases, C–C > C–N > C–O > C–H.

It is interesting to note that the $E_{\text{int}}^{0}$ of the C–O pair has a value of 1.13 eV on Pd, which is almost twice as big as that on Rh(111) (0.65 eV). This is well consistent with what we have found for the barrier reduction in CO dissociation from the flat surfaces to the steps: on Pd it is 1.30 eV, which is nearly twice as big as that on Rh (0.70 eV). Therefore, the larger barrier reduction on Pd as compared to Rh can be attributed to its larger $E_{\text{int}}^{0}$, a consequence of the bonding competition effect. For the CH$_4$ ↔ CH$_3$ + H reaction, we can use Figure 5 to understand why the $E_{\text{int}}^{\text{TS}}$ of CH$_4$ ↔ CH$_3$ + H is so small, only 0.2 eV (Table 5). Both CH$_3$ and H only have one valency, and thus they do not induce a large bonding competition effect.

4.4. Where a Catalytic Reaction Should Occur: A General Discussion. From the above results, the following rules can be generalized regarding where a catalytic reaction should occur: (i) Dissociation reactions always occur preferentially on surface defects. (ii) Association reactions with higher-valency reactants are more likely to occur on surface defects than those with lower-valency reactants. (iii) Association reactions on the later transition metals, such as Pd and Pt, are more structure-sensitive than those on the earlier transition metals.

These rules can be used to explain why ammonia synthesis is highly structure-sensitive: one of the most important elementary steps in ammonia synthesis is the N$_2$ dissociation in which the product, N atom, possesses a high valency. According to the rules above, the N$_2$ dissociation should be structure-sensitive (prefer to occur on steps), which is consistent with experiment. The fact that the Fischer–Tropsch synthesis, for example, on Co, is structure-sensitive may also be explained. Our recent calculations have shown that the barriers for C/C coupling reactions on Ru, such as C + CH and C + CH$_2$ in which one of the reactants (i.e., C) possess high valency, are much lower on steps than those on flat surfaces. For the same reason, association reactions involving H atoms (small valency), that is, hydrogenation reactions, are structure-insensitive. In other

![Figure 5. The calculated $E_{\text{int}}^{0}$ for different atomic pairs on Ru(0001), Rh(111), and Pd(111) using eq 5.](image-url)

words, the barriers of hydrogenation reactions on flat surfaces will be similar to those on steps.

Finally, it is interesting to discuss the structure effect of CO oxidation on metals. As mentioned in the Introduction, CO oxidation on transition metals seems not to be very sensitive to the surface structure change. The reasons are as follows: First, it belongs to the association reaction, which is quite insensitive to the electronic effect. Second, the bonding competition between CO and O atom was found to be quite small because of its TS geometry. Therefore, the barriers of CO oxidation on flat surfaces and steps of the same metal will be similar. For example, the barrier reported for CO + O → CO₂ on Pd(111) at 1/4 ML is 0.93 eV by Zhang and Hu, and on Pd-step the barrier was reported to be 1.0 eV by Hammer.51

5. Conclusions

This work represents one of the attempts to obtain a comprehensive picture of the surface structure effect on catalytic reactions. Two types of reactions, CH₄ + O → C + 0 or O₂ + C → C + O, on two transition metal surfaces were chosen as model systems aiming to address in general where a catalytic reaction should occur. The dissociations of CH₄ → CH₃ + H and CO → C + O and their reverse reactions on flat, stepped, and kinked Rh and Pd surfaces were studied in detail. The reaction pathways and reaction barriers were calculated. The following conclusions regarding chemisorption energies of reactants and reaction barriers are obtained:

(i) The H chemisorption energy on the flat Rh(111) is 2.92 eV, which is very similar to the H chemisorption energies on the Rh-step and the Rh-kink. On the flat Pd(111), Pd-step, and Pd-kink, the H chemisorption energies are also similar (3.05 eV).

(ii) The CH₃ chemisorption energy on the flat Rh(111) is 1.88 eV, and on the Rh-step and the Rh-kink the chemisorption energies are identical (2.16 eV) and slightly larger than that on the flat surface. On Pd surfaces, the CH₃ chemisorption energy is in the following order: Pd-step (2.01 eV) > Pd-kink (1.88 eV) > Pd(111) (1.78 eV).

(iii) The CH₄ dissociation barrier on the flat Rh(111) is 0.67 eV. The barriers on the Rh-step and Rh-kink are similar (0.32 and 0.20 eV, respectively), but significantly lower than that on the flat Rh(111). Similarly, on Pd the CH₄ dissociation barrier is reduced by ~0.3 eV from the flat surface (0.66 eV) to the steps (0.38 eV) and kinks (0.41 eV).

(iv) The CO dissociation barrier on the flat Rh(111) is 1.17 eV, and it is dramatically reduced on the Rh-step (0.3 eV) and the Rh-kink (0.21 eV). On Pd(111), the CO dissociation barrier is very high (1.87 eV). Again, the barriers on the Pd-step (0.57 eV) and the Pd-kink (0.38 eV) are much lower than that on the flat Pd(111). The TSs for CO dissociation on the flat surfaces involve four metal atoms, and the C and O share bonding with one metal atom, while the TSs involve five atoms on steps and kinks with no metal atoms being shared.

(v) The association barriers of CH₃ + H on the flat Rh(111), the Rh-step, and the Rh-kink are very similar (0.65, 0.59, and 0.49 eV, respectively). They are also similar to that on the Pd(111), the Pd-step, and the Pd-kink (0.68, 0.63, 0.53 eV, respectively). In contrast, the association barriers of the C + O on the flat surfaces are very different from those on steps and kinks. On the flat Rh(111) and Pd(111), the barriers of C + O are 1.84 and 1.98 eV, respectively. On the Rh-step and Rh-kink, the barriers are similar (1.18 and 1.09 eV, respectively), but are significantly lower than that on the flat Rh(111). This is also true for the barriers on the Pd-step and Pd-kink (0.68 and 0.49 eV, respectively).

On the basis of our reaction barrier decomposition, we obtain the following understanding of the barrier on different sites:

(i) For CH₄ dissociation, the reduction of the barrier by ~0.3 eV on the steps as compared to on the flat surfaces is mainly due to the local electronic effect. The geometrical effect plays little role in affecting the barriers. Because of the barrier reduction on steps, steps are always favored for CH₄ dissociation. On the other hand, there is essentially no difference in barrier for the association reaction of CH₃ + H on the flat surfaces and defects, because the extent of the local electronic effect on the initial state is almost the same as that on the TS and no geometrical effect exists.

(ii) For the CO → C + O reaction, the geometrical effect is more important than the local electronic effect in reducing the barrier from the flat surfaces to the defects. The electronic effect is ~0.3 eV, while the geometrical effect is more than 0.6 eV. Because of a large amount of barrier decrease on the steps and kinks as compared to on the flat surfaces, defects are much more favored for CO dissociation. In contrast to the CH₃ + H reaction, the C + O association reaction also preferentially occurs on steps and kinks due to the geometrical effect.

Finally, we arrive at some simple rules with respect to where a reaction should occur as follows:

(i) Defects such as steps are always favored for dissociation reactions as compared to flat surfaces. In other words, dissociation reactions are structure-sensitive.

(ii) Association reactions can be either structure-sensitive or structure-insensitive. The structure-sensitivity, that is, where a reaction should occur, is largely related to the bonding competition effect, which is determined by the reactant and metal valency. First, reactions with high valency reactants are more structure-sensitive, as compared to reactions with low valency reactants. Second, the reaction on the early transition metals is less structure-sensitive than that on the late transition metals.

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