

# General trends in the barriers of catalytic reactions on transition metal surfaces

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A catalyst preparation by design is one of the ultimate goals in chemistry. The first step towards this goal is to understand the origin of reaction barriers. In this study, we have investigated several catalytic reactions on some transition metal surfaces, using density functional theory. All the reaction barriers have been determined. By detailed analyses we obtain some insight into the reaction barrier. Each barrier is related to (i) the potential energy surface of reactants on the surface, (ii) the total chemisorption energy of reactants, and (iii) the metal *d* orbital occupancy and the reactant valency. © 2001 American Institute of Physics. [DOI: 10.1063/1.1403006]

## INTRODUCTION

It is well known that catalytic, particularly, heterogeneous catalytic reactions play an important role in many processes. To date, however, the catalysts are by and large developed by trial-and-error methods. Obviously, a catalyst preparation by design is highly desirable. It has long been realized that the designing of catalysts may be achieved if catalytic reaction barriers can be predicted<sup>1-5</sup> because macroscopic reaction rates depend exponentially on the reaction barriers. The first step towards this goal is to understand the origin of reaction barriers, which remains a challenging task in chemistry. Despite tremendous efforts in the last few decades<sup>6,7</sup> there has been little success due to the volatile feature of reaction barriers, varying from zero to several electron volts. In this paper we report a systematic study of typical heterogeneous catalytic reactions on several important transition metal surfaces, using density functional theory (DFT). By detailed analyses, some important trends of reaction barriers in heterogeneous catalysis are identified.

Specifically, we have simulated the following catalytic reactions: CO oxidation,  $\text{CO} + \text{O} \rightarrow \text{CO}_2$ , on Ru(0001), Rh(111), and Pt(111) and hydrogenation,  $\text{C} + \text{H} \rightarrow \text{CH}$ ,  $\text{N} + \text{H} \rightarrow \text{NH}$  and,  $\text{O} + \text{H} \rightarrow \text{OH}$ , on Ru(0001), Rh(111), and Pd(111). These are important reactions in many fundamental catalytic processes. The calculation details are described in Ref. 8. Transition states (TSs) of the reactions were searched by constraining the distance between two reactants (i.e., OC–O distance in CO oxidation) using the so-called constrained minimization technique.<sup>1,2,9,10</sup> 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 remaining degrees of freedom.

All the reaction barriers ( $E_a$ ) were calculated and listed in Table I. As shown in Table I the values of the reaction barriers for these reactions vary considerably, from 0.68 to 1.50 eV. In order to understand the origin of reaction barriers, we have applied the following approach to analyze the

total chemisorption energy of reactants A and B at the TS,  $E_{A+B}^{\text{TS}}$ , as illustrated in Fig. 1(a),

$$E_{A+B}^{\text{TS}} = E_A^{\text{TS}} + E_B^{\text{TS}} - E_{\text{int}}^{\text{TS}}, \quad (1)$$

where  $E_A^{\text{TS}}$  is the chemisorption energy of reactant A at the TS without reactant B;  $E_B^{\text{TS}}$  is defined in a similar way; and  $E_{\text{int}}^{\text{TS}}$  is the interaction energy between A and B at the TS. The physical meaning of  $E_A^{\text{TS}}$ ,  $E_B^{\text{TS}}$  and  $E_{A+B}^{\text{TS}}$  are self-evident while  $E_{\text{int}}^{\text{TS}}$  contains several terms, including the A–B bond formation energy, the direct Pauli repulsion between A and B and the energy costs due to the weakening of surface-A bond and surface-B bond at the TS. The weakening of surface-reactant bond at the TS results mainly from an indirect surface-mediated interaction, the so-called bonding competition effect.<sup>1,11,12</sup>  $E_{\text{int}}^{\text{TS}}$  may consist of other terms, i.e., electrostatic interaction between reactant A and B, but they are believed to be very small.<sup>12</sup> Similarly, we obtain

$$E_{A+B}^{\text{IS}} = E_A^{\text{IS}} + E_B^{\text{IS}} - E_{\text{int}}^{\text{IS}} \quad (2)$$

for the initial state (IS). Then the reaction barrier  $E_a$  can be written as

$$E_a = E_{A+B}^{\text{IS}} - E_{A+B}^{\text{TS}} = \Delta E_A + \Delta E_B + \Delta E_{\text{int}}, \quad (3)$$

where  $\Delta E_A = E_A^{\text{IS}} - E_A^{\text{TS}}$ ;  $\Delta E_B = E_B^{\text{IS}} - E_B^{\text{TS}}$ ;  $\Delta E_{\text{int}} = E_{\text{int}}^{\text{IS}} - E_{\text{int}}^{\text{TS}}$ . Clearly,  $\Delta E_A$  and  $\Delta E_B$  are the energy costs of reactants A and B, respectively, moving from the IS to the TS in the absence of the other reactant. Thus we call these energies reactant-activation energies of A and B, respectively. In fact, each reactant-activation energy, say  $\Delta E_A$ , contains two components, shown in Fig. 1(b): (i) the *reactant-translation* energy ( $\Delta E_A^{\text{tran}}$ ), which is the energy difference between reactant A at the IS and at the local minimum near the TS (Ref. 13); and (ii) the *reactant-coactivation* energy ( $\Delta E_A^*$ ), which is the energy difference between reactant A at this local minimum near the TS and at the TS without B. The significance of this decomposition will be seen below. As for  $\Delta E_{\text{int}}$ , generally,  $\Delta E_{\text{int}} \approx E_{\text{int}}^{\text{TS}}$ . This is due to the fact that the interaction energy at the IS,  $E_{\text{int}}^{\text{IS}}$ , is usually very small (less than 0.1 eV from our calculations) at low and medium coverages (large separation between two reactants). Obviously,

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TABLE I. Reaction barriers of CO oxidation (defined as Class I, see text) and hydrogenation (Class II) and their decompositions from DFT calculations. Each term in the table is defined in the text [see Eq. (3)]. In the hydrogenation reactions,  $\Delta E_H$  is different from the H-coactivation energy.  $\Delta E_H^* (= \Delta E_H - \Delta E_H^{\text{tran}})$  due to the H-translation energy ( $\Delta E_H^{\text{tran}}$ ) is not zero (see Ref. 13).  $\Delta E_H^{\text{tran}}$  was calculated to be 0.24, 0.44, and 0.58 eV on Ru(0001), Rh(111), and Pd(111) surfaces, respectively. As to others,  $\Delta E_{\text{CO}} = \Delta E_{\text{CO}}^*$ ,  $\Delta E_{\text{O}} = \Delta E_{\text{O}}^*$  and  $\Delta E_{\text{R}} = \Delta E_{\text{R}}^*$  (see Refs. 13, 15). In the CO oxidation reactions, the surface relaxation effect has also been included in  $E_a$ , but not listed in this table since their contribution to  $E_a$  is found to be small (less than 0.1 eV). The unit of energies is eV.

Class I		$\Delta E_{\text{O}} (\Delta E_{\text{O}}^*)$	$\Delta E_{\text{CO}} (\Delta E_{\text{CO}}^*)$	$\Delta E_{\text{int}}$	$E_a$
CO oxidation	Pt(111)	0.70	0.15	0.03	0.80
	Rh(111)	0.62	0.44	-0.09	0.94
	Ru(0001)	0.89	0.53	0.08	1.45
Class II		$\Delta E_{\text{R}} (\Delta E_{\text{R}}^*)$	$\Delta E_{\text{H}} / \Delta E_{\text{H}}^*$	$\Delta E_{\text{int}}$	$E_a$
Hydrogenation on Ru(0001)	C	0.03	0.30/0.06	0.35	0.68
	N	0.08	0.32/0.08	0.67	1.08
	O	0.12	0.33/0.09	1.01	1.46
Hydrogenation on Rh(111)	C	0.02	0.44/0.00	0.26	0.72
	N	0.05	0.45/0.01	0.49	0.99
Hydrogenation on Pd(111)	O	0.08	0.43/-0.01	0.84	1.36
	C	0.05	0.60/0.02	0.51	1.16
	N	0.05	0.59/0.01	0.67	1.31
	O	0.11	0.59/0.01	0.80	1.50

$\Delta E_{\text{int}}(E_{\text{int}}^{\text{TS}})$  is strongly related to the TS geometry. We expect that some reactions may have such TS structures that their  $E_{\text{int}}^{\text{TS}}$  may be very small. In this case, Eq. (3) can be approximated as  $E_a \approx \Delta E_A + \Delta E_B$ , which means that the reaction barrier will be dominated by the reactant-activation energies. On the other hand, for other reactions  $E_a$  may be strongly related to  $E_{\text{int}}^{\text{TS}}$ , if  $E_{\text{int}}^{\text{TS}}$  is significant.

Using this DFT decomposition approach [Eq. (3)] for all the reactions investigated in this study (Table I), we have indeed found that the seemingly complicated reactions can be divided into two simple classes and the reaction barriers of each class follow simple rules. Class I:  $E_{\text{int}}^{\text{TS}}$  can be neglected. All the CO oxidation reactions investigated belong to this class. Class II:  $E_{\text{int}}^{\text{TS}}$  is significant. All the hydrogenation reactions investigated belong to this class. Since the physical origins of the reaction barriers in these two classes are rather different, we discuss each class in turn.

### CLASS I

The geometrical structure of the TS for CO oxidation is illustrated in Fig. 2(a), which shows that reactants do not significantly share bonding with surface atoms. The O is on the bridge site and the CO is on the off-top site,<sup>1,10</sup> suggesting a low bonding competition at the TS. It is not surprising, therefore, that the interaction energy differences ( $\Delta E_{\text{int}}$ ) for Class I are found to be small (less than 0.1 eV), listed in Table I. Consequently, the reaction barriers are mainly determined by the sum of the reactant-activation energies. This is illustrated by the dashed line in Fig. 3, which is plotted using  $(\Delta E_{\text{CO}} + \Delta E_{\text{O}})$  against  $E_a$ . The linear relationship implies that the higher the total reactant-activation energy, the higher the reaction barrier will be. In fact we have identified another

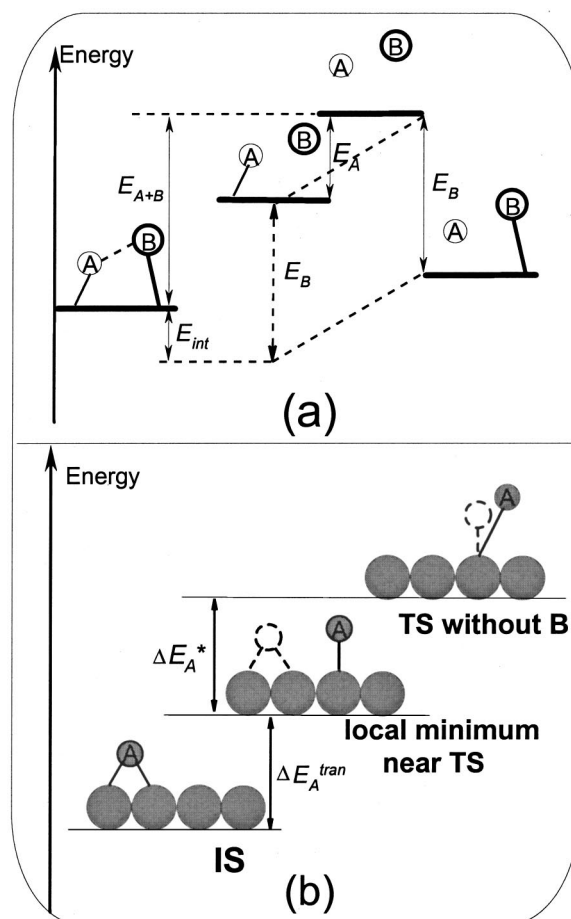


FIG. 1. (a) The energy diagram of a co-adsorption system with two adsorbates A and B. (b) Illustration of the decomposition of a reactant-activation energy, in which the reactant is on the bridge site at the IS and on the off-top site at the TS: (i) the reactant-translation energy; and (ii) the reactant-coactivation energy. All the terms in the figure are defined in the text.

linear relationship between the total chemisorption energy ( $\sum_x E_x^{\text{IS}}$ ,  $X = \text{CO}, \text{O}$ ) at the IS and the reaction barrier, which is displayed by the solid line in Fig. 3. The reactions in Class I can, therefore, be described in the following equation,

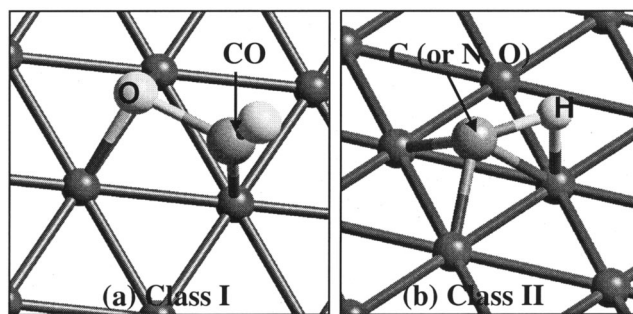


FIG. 2. Schematic illustration of TS structures. (a) Class I, illustrated by CO oxidation. No metal atoms are shared by the reactants at the TS. This class may include other reactions, such as reactions on steps, kinks, and open surfaces. (b) Class II: illustrated by hydrogenation reaction. One metal atom is shared by the reactants at the TS. For the CO oxidation, at the IS the O is at the hollow site, while CO is at top site (Refs. 1, 10). For the hydrogenation reactions, both reactants (the C, or N or O and the H atom) prefer hollow sites at the IS (Ref. 2).

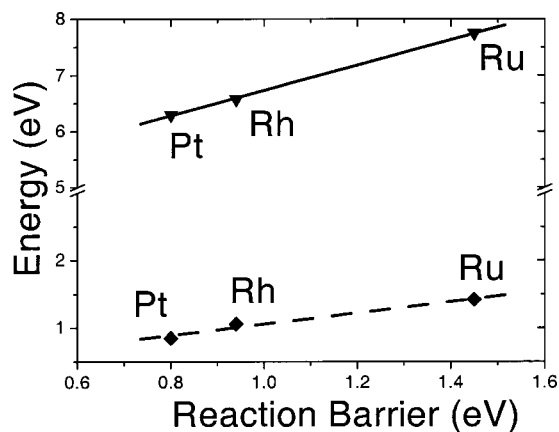


FIG. 3. Illustration of the CO oxidation barrier as a linear function of the total reactant-activation energy ( $\Delta E_{\text{O}} + \Delta E_{\text{CO}}$ ) (dashed line) and the total chemisorption energy at the IS (solid line) on Ru, Rh, and Pt. As can be seen,  $E_a \approx \Delta E_{\text{O}} + \Delta E_{\text{CO}} \propto \sum_X E_X^{\text{IS}}$ .

$$E_a \approx \Delta E_{\text{CO}} + \Delta E_{\text{O}} \propto \sum_X E_X^{\text{IS}}. \quad (4)$$

## CLASS II

Figure 2(b) illustrates the geometrical structure of the TSs for Class II reactions (hydrogenation). Clearly, one metal atom is shared by reactants. In contrast to Class I, the reactant-activation energies [ $\Delta E_{\text{H}}$  and  $\Delta E_{\text{R}}$  ( $R = \text{C, N, O}$ )] remain almost constant (Table I). However, the interaction energy differences,  $\Delta E_{\text{int}}$ , are significant and vary, which may not be surprising, considering the fact that the two reactants now share bonding with a metal atom at the TSs. The so-called bonding competition effect<sup>1,12</sup> will reduce the reactant chemisorption energies and thus increase the interaction energy. As shown in Table I, on the same metal surface,  $\Delta E_{\text{int}}$  (also  $E_a$ ) will increase proportionally as the  $R$  valency decreases. This relationship is illustrated in Fig. 4, which reveals that  $E_a$  is a linear function of the reactant valency.

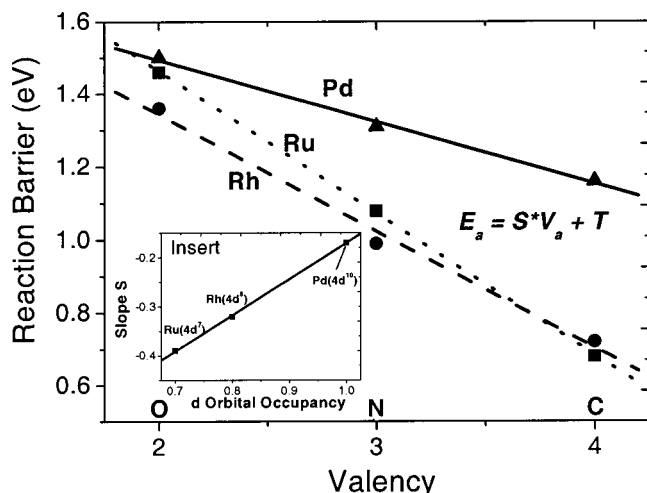


FIG. 4. Illustration of the hydrogenation reaction barriers as linear functions of the valency ( $V_a$ ) of the reaction counterpart to H (C, N, O) on Ru, Rh, and Pd:  $E_a = S \times V_a + T$ . The insert shows that the slope,  $S$ , is a linear function of metal  $d$  orbital occupancy.

This valency rule is consistent with chemical intuition. It is expected that the more valence electrons the adsorbate has, the closer to a closed-shell configuration it is and the larger Pauli repulsion it has on the other reactant. Therefore, we arrive at

$$E_a = S \times V_a + T, \quad (5)$$

where  $V_a$  is the valency of reactant (C, N, O),  $S$  (negative) and  $T$  (positive) represent the slope and intercept, respectively. On going from one metal surface to another, we found that metals also affect  $\Delta E_{\text{int}}$ . The slope  $S$  in Eq. (5) is a linear function (correlation coefficient: 1.00) of metal  $d$  orbital occupancy ( $M_d$ ) [ $S = p \times M_d + q$ ,  $p$  (positive) and  $q$  (negative) are constants], as illustrated in the insert of Fig. 4.  $M_d$  is 0.7, 0.8, and 1.0 for Ru, Rh, and Pd (atomic  $d$  configuration), respectively.<sup>14</sup> Combining this with Eq. (5), we obtain

$$E_a = (p \times M_d + q) \times V_a + T. \quad (6)$$

It should be emphasized that the reaction barriers in Class II contain two parts. The first part,  $(p \times M_d + q) \times V_a$ , is negative, which increases with the metal  $d$  occupancy and decreases with the reactant valency. The second part,  $T$ , is larger and positive, and is a metal-dependent constant.

## COMPARISON BETWEEN CLASS I AND CLASS II REACTIONS

A striking difference between the CO oxidation (Class I) and the hydrogenation reactions (Class II) is that  $E_a$  in Class I reactions is related to the total chemisorption energy of reactants at the IS, while  $E_a$  in Class II varies strongly with the reactant valency and the metal  $d$  orbital occupancy. An analysis of these reactions using Eq. (3) may provide some clues as to why this is so. In the CO oxidation reactions,  $\Delta E_{\text{int}} (\approx E_{\text{int}}^{\text{TS}})$  is negligible and thus  $E_a$  is almost purely determined by the reactant-activation energies ( $\Delta E_{\text{CO}}$  and  $\Delta E_{\text{O}}$ ). Since the reactant-translation energies for both CO and O are zero in the CO oxidation investigated here,<sup>15</sup>  $E_a$  is in fact determined by the reactant-coactivation energies,  $\Delta E_{\text{CO}}^*$  and  $\Delta E_{\text{O}}^*$ . Therefore, it is the total reactants-coactivation energy,  $\Delta E_{\text{CO}}^* + \Delta E_{\text{O}}^* (= \Delta E_{\text{CO}} + \Delta E_{\text{O}} \approx E_a)$ , that closely relates to  $\sum_X E_X^{\text{IS}}$ , the initial chemisorption energies (as illustrated in Fig. 3), which is consistent with chemical intuition, the stronger the reactants adsorb, the more difficult the activation. In contrast to the CO oxidation, in the hydrogenation reactions  $\Delta E_{\text{int}} (E_{\text{int}}^{\text{TS}})$  that is related to the reactant valency and metal properties is significant and determines the trends of  $E_a$ . With respect to the reactant-activation energy terms,  $\Delta E_{\text{R}}$  is always very small (around 0.1 eV), and only  $\Delta E_{\text{H}}$  has a reasonable contribution to  $E_a$  (Table I). Furthermore, we have found that  $\Delta E_{\text{H}}$  is mainly determined by the H-translation energy [ $\Delta E_{\text{H}}^{\text{tran}}$ , the energy cost for H moving from a hollow site (IS) to a top site (local minimum near the TS)].<sup>13</sup> Subtracting  $\Delta E_{\text{H}}^{\text{tran}}$  from  $\Delta E_{\text{H}}$ , the H-coactivation energy,  $\Delta E_{\text{H}}^*$ , is found to be quite small (Table I). It should be noted that the reactant-translation energies for  $R$  (C, N, O) are zero,<sup>13</sup> i.e.,  $\Delta E_{\text{R}} = \Delta E_{\text{R}}^*$ . Thus, the total reactants-coactivation energies ( $\Delta E_{\text{H}}^* + \Delta E_{\text{R}}^*$ ) contribute little to  $E_a$  in the hydrogenation reactions, which is, interestingly, again just opposite to that in the CO oxidation.



Therefore, it is reasonable that in Class II no obvious correlation between  $E_a$  and the initial chemisorption energies is found.

We expect that many simple reactions in heterogeneous catalysis may belong to one of these two classes.<sup>16</sup> Class I reactions are not limited to CO oxidation and should include other reactions in heterogeneous catalysis, such as reactions on corrugated surface [e.g., NO, N<sub>2</sub> dissociation on stepped Ru(0001)]<sup>17,18</sup> and on more open surfaces [e.g., C–H bond activation on (110) surface].<sup>19</sup> For close packed metal surfaces, however, we find that most reactions belong to Class II.<sup>2,11</sup> In fact, the understanding provided above may facilitate the explanation of many important observations in this field. For example, it is well known that the surface structure effect is an important issue in catalysis. The barrier of many surface reactions, particularly dissociation reactions, can be reduced on steps or kinks.<sup>11</sup> This may result from the fact that on these sites reactions are likely to occur via the Class I mechanism, i.e., no surface atom being shared by reactants, which leads to the interaction energy ( $E_{\text{int}}^{\text{TS}}$ ) being greatly reduced. Therefore, the total energies of the TSs are decreased and so are the reaction barriers. Another example is the different reactivities of metals for CO oxidation. Ru, for instance, is notably inert for CO oxidation at low and medium O coverages while Pt is an excellent catalyst for the reaction. The current view is that in order for CO oxidation to occur, the O must be activated.<sup>1,9,10,20,21</sup> Since O–Ru bond is much stronger than O–Pt, Ru is much less reactive than Pt. The major difficulty using this simple argument is that the activation energies of O from the ISs to the TSs are very similar on different metal surfaces (see Table I). Therefore  $\Delta E_{\text{O}}$  alone is not sufficient to explain the reactivity difference. However, the reactivity difference can be explained using our results. As can be clearly seen in Table I, the CO-activation energies,  $\Delta E_{\text{CO}}$ , on different metals varies considerably. It is  $\Delta E_{\text{CO}}$  that gives rise to different reactivity of metal for CO oxidation. The significance of the CO activation was also noted by Glassey and Hoffmann<sup>22</sup> very recently.

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<sup>13</sup>The local minimum near the TS is defined in order to differentiate it from the global minimum for a reactant on a surface (although the two minima may be same for the reactant in some reactions). For instance, in the hydrogenation reaction the H atom sits on a hollow site at the IS and it is close to a top site at the TS. Thus, the local minimum near the TS for the H atom is the top site.

<sup>14</sup>It is worth mentioning that a linear function can still be obtained if the bulk  $d$  occupancy is plotted against the slope  $S$ , but with a smaller correlation coefficient (0.98). This result indicates that the surface atoms involved in the reaction are more atomlike than bulklike. There could be two reasons for this: (i) surface atoms are less coordinated compared to bulk atoms; or (ii) the metal–metal bonding is further weakened due to the adsorption. Therefore, it is not surprising that the surface atoms involved in the reaction are quite different from bulk atoms.

<sup>15</sup>In the CO oxidation investigated on Ru, Rh, and Pd surfaces, the reactant-translation energies of both CO and O are zero since at the IS the most stable adsorption sites are top sites and hollow sites (see Fig. 2 caption) for CO and O, respectively. It should be mentioned that for CO oxidation on Pd(111) at low coverage CO prefers a hollow site at the IS and sits on the off-top site at the TS. Thus, in this case CO-transition energy that is the energy difference between CO at the hollow site and at the top site (about 0.7 eV), contributes significantly to the reaction barrier.

<sup>16</sup>Our recent calculations for the same hydrogenation reactions on  $5d$  metals [Os(0001), Ir(111), and Pt(111)] have shown that the model presented here can be successfully applied to  $5d$  metals.

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