

Analysis of methane-to-methanol conversion on clean and defective Rh surfaces

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(Received 27 February 2006; accepted 7 June 2006; published online 24 July 2006)

We investigate by density-functional theory simulations several elementary reactions associated to direct methane-to-methanol conversion on clean Rh(111) surfaces and on Rh adatoms on Rh(111). Energy barriers and reaction paths have been determined by the nudged elastic band method. The rate-limiting step in the process, C–O bond formation, has higher activation energy than the one for complete methane dehydrogenation. Our analysis enables us to understand the effect of defects on the reactivity and rules out Rh as candidate catalyst for methanol synthesis. © 2006 American Institute of Physics. [DOI: [10.1063/1.2219448](https://doi.org/10.1063/1.2219448)]

I. INTRODUCTION

Large amount of methane (CH₄) are wasted or not exploited due to difficulty in transportation and storage. Efficient conversion to an easily transportable liquid such as methanol (CH₃OH) would be highly desirable. Traditional industrial production of methanol from methane is based on two high-temperature steps: syngas (a CO and H₂ mixture) is first formed via steam reforming of methane, and finally methanol is synthesized from it. The process is very energy consuming and not economically convenient for large scale production of methanol, e.g., as fuel alternative. Alternatively, direct low-temperature conversion of CH₄ to CH₃OH in the presence of O₂ has been proposed. This process, whose net reaction reads



could have the advantage of being exothermic, so that no wasted energy is required to drive the reaction.

Gas-phase methane-to-methanol conversion is operated by a free radical mechanism which is hard to control.¹ The participation of a catalyst to the reaction is expected to improve methanol yield and selectivity, but despite several attempts, no adequate catalyst has been found yet to compete with the direct process. Following the observation that gas-phase FeO⁺ can convert methane to methanol,² catalysis operated by transition metal cations has been studied extensively.^{3–6} Promising results have also been obtained in the homogeneous liquid phase in concentrated sulfuric acid,^{7,8} but there are still concerns about costs, environmental aspects, and the use of relatively high temperatures. To our knowledge, no detailed study has been presented yet for the case of heterogeneous catalysis by transition metal surfaces.

These surfaces can effectively activate C–H bonds in methane. A major problem in this context is, however, the tendency of dehydrogenation to proceed until graphite is

eventually formed on the surface. It has been shown for Ni(111),⁹ Ru(0001),¹⁰ and Pd(001) (Ref. 11) surfaces that if a catalyst is able to break one C–H bond to make methyl radicals available, then it will also break all the other C–H bonds (possibly with the exception of the last one in CH), quickly resulting in coking and poisoning of the catalyst.

Recently it was shown theoretically that the presence of Rh adatoms on Rh(111) surfaces can enhance the first dehydrogenation of CH₄ while hindering the further decomposition of CH₃.¹² The activation energies for these two processes were estimated to be 0.69 and 0.42 eV on the clean surface and 0.47 and 0.63 eV at the adatom site. Moreover methane was found to preferentially adsorb at the adatom site by as much as 0.2 eV. Thus it should be possible to tune the temperature so that methane is activated at an adatom site, but no further dehydrogenation occurs. Similar theoretical findings were reported for single Pt adatom on MoO₃(010) surface.¹³ This suggests adatoms as promising model reaction sites for various chemical synthesis and, in particular, methane-to-methanol conversion.

In this article we will thoroughly investigate by means of density-functional theory simulations the possible pathways of methane-to-methanol conversion on clean Rh(111) surfaces and on Rh adatoms on Rh(111) [henceforth referred to as Rh/Rh(111)], in order to highlight the effect of low reaction-site coordination. The energy of the stable intermediates and the activation barriers of several elementary reaction steps will be determined by the nudged elastic band algorithm.¹⁴ The rate-limiting steps of the conversion will be identified for the two substrates and their activation energies compared with the one of the competing process—CH₃ further dehydrogenation—leading to catalyst coking and inactivation.

In order to extend the validity of our results to more generic Rh catalysts, the sensitivity of activation barriers to reaction-site geometry will be discussed, critically reexamining the arguments recently put forward by Liu and Hu in Ref. 15.

Based on this analysis we conclude that Rh systems are

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unfortunately not expected to be suitable catalysts for low-temperature methane-to-methanol conversion.

II. COMPUTATIONAL METHOD

All calculations presented here have been performed within the framework of density-functional theory (DFT) employing the Perdew-Burke-Ernzerhof¹⁶ (PBE) generalized gradient approximation (GGA) for the exchange and correlation functional. A three-layer slab was used to model the Rh(111) surface. The bottom two layers were kept fixed at the bulk-truncated positions, while the upper one was allowed to relax. Molecules were placed on this side of the slab and relaxed together with the upper layer until the forces on the atoms were less than 0.02 eV/Å, even though adsorption energies were well converged already using a threshold of 0.05 eV/Å. We restricted our analysis to a coverage of 0.25 ML, using a (2×2) surface unit cell. The plane-wave ultrasoft pseudopotential method¹⁷ was used as implemented in the PWSCF code of the Quantum-ESPRESSO distribution.¹⁸ A kinetic energy cutoff of 27 Ry and 60 special points for the Brillouin zone (BZ) integration¹⁹ were considered in the bulk fcc unit cell. The same cutoff and equivalent **k**-point meshes were used for all the surface structures investigated in this article. Test calculations with a lower (25 Ry) kinetic energy cutoff and a BZ sampling twice as coarse as above have also been performed for all the metastable structures studied, and the root mean square error found for the adsorption energies was less than 0.07 eV.

Activation barriers for transitions from one metastable configuration to another have been computed using the climbing-image nudged elastic band (NEB) method,¹⁴ which allows us to identify the transition state of a given process. Reaction paths were optimized until the norm of the forces at the transition states was less than 0.05 eV/Å.

Using the above setup, we obtained for fcc bulk Rh a lattice constant $a_0=3.86$ Å and a bulk modulus $B=255$ GPa. In agreement with typical results obtained within GGA approximation theoretical lattice parameter is slightly overestimated and the bulk modulus underestimated with respect to experimental results [3.80 Å (Ref. 20) and 269 GPa,²¹ respectively].

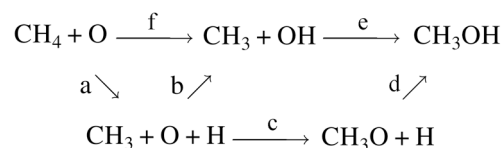
Total energies of isolated molecules and atoms, needed as reference to compute adsorption energies, have been evaluated in a cubic cell of 20 bohrs side length using Γ point only for Brillouin zone integration, and allowing for spin polarization. The net reaction from methane and oxygen to methanol is found exothermic by 1.36 eV, in good agreement with accurate Gaussian-2 value with zero-point vibrations removed [1.49 eV (Ref. 22)]. Larger errors are obtained in other cases. As for atomization energy of O₂ molecule, we obtain 5.49 eV rather than 5.12 eV.³⁶

III. OVERVIEW OF THE SYSTEM

Adsorption of oxygen on Rh surfaces has been studied extensively experimentally,^{23–25} theoretically,^{26,27} and by combined approaches.^{28,29} Oxygen molecules adsorb dissociatively on Rh(111) surface and desorb with a large activation energy [2.42 eV (Ref. 23)]. Hence, in the presence of O₂

in the gas phase the surface is readily covered by O atoms. Actually, if exposure to oxygen is high, the formation of a thin oxide layer is observed, as shown in Ref. 28. We will consider in the following the case of Rh under low oxygen exposure, hence still retaining the metallic character.

Let us examine schematically the reaction mechanisms that could lead to methanol synthesis. In the presence of atomic O, methane could, in principle, directly form methanol (CH₃OH) by “insertion” of an O atom in one of its four C–H bonds. However, the calculated value for the corresponding activation barrier is very high (2.06 eV) and this process is therefore not convenient with respect to methane decomposition. Alternatively, CH₄ could dissociate at a surface site to form CH₃ and H, or do the same on top of an adsorbed oxygen giving adsorbed CH₃ and OH. In the former case CH₃ could then combine with adsorbed oxygen to give a methoxy intermediate, CH₃O. Methanol could be subsequently formed by recombination of CH₃O and H, or OH and CH₃. These reactions, leading to methanol formation, are pictorially represented in the following diagram, where the different processes are labeled from (a) to (f) for future reference:



These reactions are in competition with other processes, leading to the complete dissociation of methane and eventually to coking and inactivation of the substrate. As mentioned previously, Kokalj *et al.*¹² have found that the activation barrier for deprotonation of CH₃ radical is 0.63 eV at an adatom site, higher than its value on the clean Rh(111) surface (0.42 eV). For direct methanol synthesis to be achievable on Rh surfaces it is necessary that for at least one path in the above diagram all intermediate and transition states involved have lower energies.

We report in Fig. 1(a) the energy profile for the above reactions occurring on the clean Rh(111) surface. The energy of desorbed methanol is chosen as reference for this diagram.

The activation energy for recombination of CH₃ and O [process (c) above] has been calculated without the additional hydrogen atom nearby, since H and CH₃ are very mobile on the surface (our estimates are 0.11 eV for the H diffusion barrier and 0.13 eV for CH₃). In a similar way, the formation of an OH group from O and H [process (b) in the diagram] has been computed in the absence of a spectator CH₃ radical.

From the results of Fig. 1(a), we see that the highest activation energies are those associated to CH₃–O and CH₃–OH bond formation. Hence, C–O bond formation is the most difficult step in methanol synthesis. The first barrier is lower than the second one (1.56 and 1.80 eV, respectively), and so the minimum energy pathway connecting methane to methanol on Rh(111) involves the following

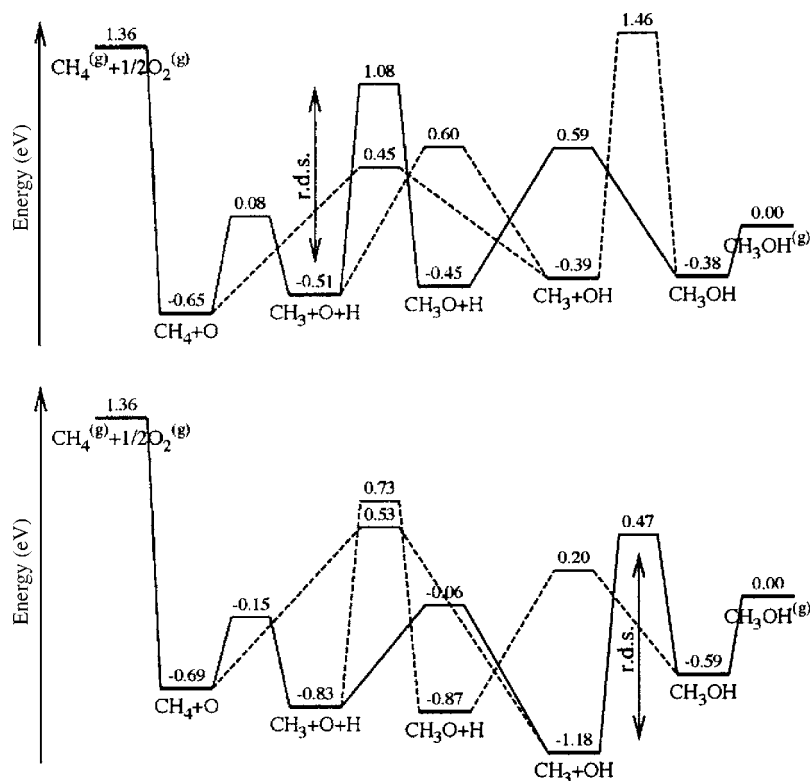


FIG. 1. Metastable configurations and transition states for reactions connecting methane to methanol. Energies are expressed in eV with respect to desorbed methanol. The solid lines indicate the minimum energy pathway going from CH_4 to CH_3OH , and the vertical arrows marked “r.d.s.” the rate-determining step. (a) Reactions occurring on the perfect Rh(111) surface. (b) The same on a Rh adatom on Rh(111).

elementary steps: dissociation of CH_4 , recombination of CH_3 and preadsorbed O, and recombination of CH_3O and H [(a)-(c)-(d) pathway].

Transition state (TS) geometries of these reactions are shown in Figs. 2(a)–2(f).

The results for the same reactions occurring at an adatom site have been collected in Fig. 1(b), and corresponding TS geometries can be found in Figs. 2(a')–2(f').

As one expects, the larger reactivity of the low-coordination Rh atom causes an increase in the binding strength of the various configurations, and the reaction pathways are lowered in energy. We notice that, moving to the adatom site, the first dehydrogenation barrier of methane decreases by 0.2 eV, in agreement with Ref. 12. Again, $\text{CH}_3\text{--O}$ association reaction has been studied in the absence of a spectator hydrogen atom, while for O–H recombination the presence of a CH_3 group at the adatom site has been considered since CH_3 strongly binds to it (adsorption stronger by 0.40 eV with respect to terrace site). In the most convenient initial configuration for this reaction, oxygen atom was bound to the adatom while H came from the terrace. This required the use of a larger (2×3) surface unit cell.

As in the case of reactions occurring at terrace sites, also

in this case the highest activation energies are associated to C–O bond formation: the barrier for $\text{CH}_3\text{--O}$ recombination (1.56 eV) is almost unaffected by the different geometry, and the one for $\text{CH}_3\text{--OH}$ lowers from 1.80 to 1.65 eV. Even if this second activation barrier is higher than the first one, this is compensated by the higher stability of $\text{CH}_3 + \text{OH}$ as compared to $\text{CH}_3 + \text{O} + \text{H}$. As a consequence, the minimum energy pathway for methane-to-methanol conversion on an adatom site goes through (a)-(b)-(e); steps: dissociation of CH_4 , recombination of H and O, and recombination of CH_3 and OH.

Coming now to the comparison with the competing CH_3 deprotonation process, it is clear that in spite of the observed stabilization of the intermediates and general reduction of most of the barriers at adatom site, the activation energies for $\text{CH}_3\text{--O}$ and $\text{CH}_3\text{--OH}$ recombination are too high with respect to those of CH_3 deprotonation, both at terrace and adatom site (0.42 and 0.63 eV, respectively).

As a consequence, the perfect Rh(111) surface and the adatom of Rh on Rh(111) are not good candidate catalysts for methane-to-methanol conversion. In particular, for the Rh/Rh(111) system, it would be possible to choose a tem-

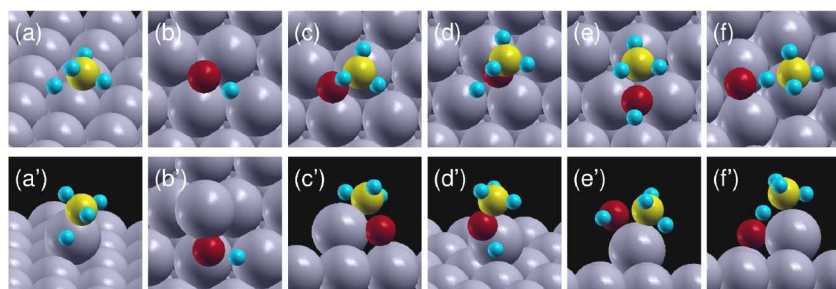


FIG. 2. (Color online) Geometry of the transition states for reactions considered in this study. On the perfect surface: (a) $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$, (b) $\text{OH} \rightleftharpoons \text{O} + \text{H}$, (c) $\text{CH}_3\text{O} \rightleftharpoons \text{CH}_3 + \text{O}$, (d) $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O} + \text{H}$, (e) $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3 + \text{OH}$, and (f) $\text{CH}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{OH}$. Panels (a')–(f'): the same as (a)–(f) on a Rh adatom.

perature for which CH_4 dissociates and CH_3 does not, but then methyl would not be able to react with O or OH.

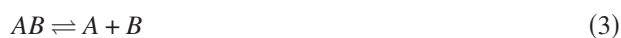
IV. DISCUSSION

In the preceding section we have examined the possible pathways that could lead to methanol formation on clean Rh(111) surface as well as on Rh adatom site on Rh(111). We have found that rate-limiting steps involve C–O bond formation. This is consistent with similar results reported in Refs. 30 and 31 for methanol decomposition on Pt(111). The C–O bond activation energy exceeds by a large amount that of the competing process where methyl radical is further deprotonated. Methanol formation is therefore not a competitive process on this surface. Since any theoretical analysis is necessarily limited in the number of systems addressed, an important issue to be understood is whether and how much our results could change considering different orientations of the substrate, some other defected structure (such as, for instance, stepped surfaces), or different chemical environment such as higher oxygen coverage. This issue has been addressed recently by Liu and Hu in Ref. 15 where general rules for predicting the reaction-site sensitivity or insensitivity for association/dissociation reactions have been proposed, based on the analysis of two simple reactions: methane first dehydrogenation and carbon monoxide dissociation. Here we critically reanalyze the arguments presented in Ref. 15 applying them to all the six reactions previously described with the exception of



which is not an association/dissociation reaction.

In their analysis, Liu and Hu¹⁵ noticed that many important dissociation reactions of generic form



have late TSs, that is, transition states close to the dissociated final state (FS). Inspection of Fig. 2 shows that this is indeed the case for the reactions considered here [with the already mentioned exception of reaction (f)]. For late-TS reactions Liu and Hu suggest that the direct (dissociation) reaction is in general reaction-site sensitive while the inverse (association) reaction is rather reaction-site insensitive. Their argument goes as follows.

The adsorption energy of $A+B$ activated complex at the TS is decomposed as

$$E_{A+B}^{\text{TS}} = E_A^{\text{TS}} + E_B^{\text{TS}} + E_{\text{int}}^{\text{TS}} = \sum E^{\text{TS}} + E_{\text{int}}^{\text{TS}}, \quad (4)$$

where E_A^{TS} (E_B^{TS}) is the adsorption energy of A (B) in the geometry of the TS without B (A), and the interaction energy $E_{\text{int}}^{\text{TS}}$ is defined by the above equation and is due to bond sharing, Pauli repulsion, and electrostatic interaction between A and B in the TS geometry. In this notation, more negative adsorption energies indicate stronger bonds. Similarly the energy of the FS can be decomposed as

$$E_{A+B}^{\text{FS}} = E_A^{\text{FS}} + E_B^{\text{FS}} + E_{\text{int}}^{\text{FS}} = \sum E^{\text{FS}} + E_{\text{int}}^{\text{FS}}, \quad (5)$$

where E_A^{FS} (E_B^{FS}) are the relaxed adsorption energies of A (B) on the substrate and $E_{\text{int}}^{\text{FS}}$ describes the correction due to coad-

sorption in the FS geometry and is usually small. For the initial state (IS) the AB molecule in the gas phase has been assumed in Ref. 15.

The dissociation reaction barrier is therefore

$$E_{\text{act}}^{\text{diss}} = \sum E^{\text{TS}} + E_{\text{int}}^{\text{TS}} - \Delta E_{AB}^{(\text{g})}, \quad (6)$$

where $\Delta E_{AB}^{(\text{g})} = E_{AB}^{(\text{g})} - E_A^{(\text{g})} - E_B^{(\text{g})}$ is the $A-B$ bond energy in the gas phase. As adsorption energies may strongly depend on the adsorption site, dissociation reactions are expected to be surface sensitive and particularly favored at defected sites. At defects, undercoordinated substrate atoms are present and their d band is narrower and, for late transition metals, shifted to higher energies than at the perfect surface. Thus, according to Hammer-Nørskov chemisorption model,³² adsorbates generally bind more strongly to defects: $\sum E^{\text{TS}}$ decreases, reducing the dissociation barrier on defects. [A similar analysis has been performed previously by Hammer for NO dissociation at clean and stepped Ru(0001) surfaces.³³] Notice, however, that the choice of a gas-phase reference in Ref. 15 ignores completely the adsorption energy of the AB molecule that could be substantial and site dependent. A more appropriate definition of the dissociation barrier is in our opinion

$$E_{\text{act}}^{\text{diss}} = \sum E^{\text{TS}} + E_{\text{int}}^{\text{TS}} - E_{AB}^{\text{IS}} - \Delta E_{AB}^{(\text{g})}, \quad (7)$$

where E_{AB}^{IS} is the molecular adsorption energy in the initial state. We will come back to this point later.

The association reaction barrier is instead defined as

$$E_{\text{act}}^{\text{ass}} = \sum E^{\text{TS}} - \sum E^{\text{FS}} + E_{\text{int}}^{\text{TS}} - E_{\text{int}}^{\text{FS}}. \quad (8)$$

For late-TS reactions, the first two terms in the right-hand side of this expression should be similar and largely compensate each other, while the last term is usually small. Surface sensitivity of association reaction depends therefore mainly on $E_{\text{int}}^{\text{TS}}$, which increases with the number of chemical bonds which are formed by reactants.¹⁵ Most species concerned here form only single bonds (e.g., $-\text{CH}_3$, $\text{CH}_3\text{O}-$, ...), so this term should be generally small.

Let us analyze in detail the five dissociation/association reactions involved in methane-to-methanol conversion on the basis of the above discussion. The relevant quantities are collected in Table I. In order to simplify the comparison between terrace and adatom sites, for both sites “spectator” radicals will not be included when examining (b) and (c) elementary processes. As a consequence, activation energies reported in Table I for these reactions are sometimes marginally different from the ones used in Fig. 1.

A. $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$

The dissociation of CH_4 to CH_3 and H, and the corresponding association reaction, is one of the two reactions investigated by Liu and Hu¹⁵ to assess the validity of their “general rules.” They reported a strong reduction of the dissociation barrier, computed according to Eq. (6), on Rh steps (0.32 eV) as compared to (111) terrace sites (0.67 eV). According to their calculation, at the step edge $\sum E^{\text{TS}}$ decreases by 0.3 eV, whereas $E_{\text{int}}^{\text{TS}}$ is small and almost unchanged

TABLE I. Activation energies and their decomposition for the dissociation/association reactions under investigation. $E_{\text{act}}^{\text{diss}}$ ($E_{\text{act}}^{\text{ass}}$) is the activation energy for dissociation (association) reaction, E_{AB}^{IS} is the adsorption energy of the AB molecule in the initial state (IS), ΣE^{TS} is the sum of adsorption energies of A and B at the transition state (TS) geometries and $E_{\text{int}}^{\text{TS}}$ their mutual interaction, and ΣE^{FS} and $E_{\text{int}}^{\text{FS}}$ are similar terms for the final state (FS) geometry. The products' binding energies in the gas phase are, from top to bottom, $\Delta E^{(g)} = -4.62, -4.76, -4.48, -4.55, \text{ and } -4.27$ eV.

Reaction	Substrate	$E_{\text{act}}^{\text{diss}}$	$E_{\text{act}}^{\text{ass}}$	E_{AB}^{IS}	ΣE^{TS}	$E_{\text{int}}^{\text{TS}}$	ΣE^{FS}	$E_{\text{int}}^{\text{FS}}$	$(\Sigma E^{\text{TS}} - \Sigma E^{\text{FS}})$
(a) $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$	Rh(111)	0.73	0.42	-0.10	-4.11	0.12	-4.58	0.17	0.47
	Rh/Rh(111)	0.41	0.39	-0.30	-4.35	-0.17	-5.07	0.16	0.72
(b) $\text{OH} \rightleftharpoons \text{O} + \text{H}$	Rh(111)	0.99	0.96	-2.88	-7.17	0.52	-7.76	0.15	0.59
	Rh/Rh(111)	1.03	0.66	-3.20	-7.11	0.18	-7.58	-0.02	0.47
(c) $\text{CH}_3\text{O} \rightleftharpoons \text{CH}_3 + \text{O}$	Rh(111)	1.53	1.57	-2.19	-5.76	0.61	-6.74	0.03	0.98
	Rh/Rh(111)	1.60	1.56	-2.62	-6.21	0.71	-7.06	0.00	0.85
(d) $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O} + \text{H}$	Rh(111)	0.97	0.89	-0.38	-4.25	0.29	-4.99	0.15	0.74
	Rh/Rh(111)	0.79	1.08	-0.59	-4.90	0.55	-5.51	0.08	1.61
(e) $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3 + \text{OH}$	Rh(111)	1.84	1.80	-0.38	-3.24	0.43	-4.66	0.55	1.42
	Rh/Rh(111)	1.06	1.65	-0.59	-4.35	0.55	-5.48	0.03	1.13

(0.20 eV on the flat surface and 0.16 eV at the step). Our calculated value for the dissociation barrier, according to Eq. (7), on the flat Rh(111) surface is 0.73 eV. To properly compare with Liu and Hu's result, the molecular adsorption energy should be added to this value: one obtains 0.63 eV, in excellent agreement with the result of Ref. 15.

In analogy with the reported result for step edge, we find a significant reduction of the activation energy at the adatom site (0.41 eV) that would be even stronger (0.11 eV) by taking the gas phase as a reference. We stress, however, that in the adatom case, reported here, the reason for site sensitivity of the activation barrier seems different from the one occurring at the step: as it was found for the step case the TS is stabilized at the adatom (ΣE^{TS} decreases by 0.24 eV) but this contribution to the barrier is compensated by a similar increase in CH_4 adsorption energy (0.20 eV). An essential contribution to site sensitivity for this reaction barrier comes from product interaction energy at the TS, $E_{\text{int}}^{\text{TS}}$, which, although small in absolute terms (0.12 and -0.17 eV for the terrace and the adatom, respectively), is not constant and changes by as much as 0.29 eV, favoring the adatom site. The peculiar negative sign of $E_{\text{int}}^{\text{TS}}$ at the adatom means that, at the TS geometry, the interaction is attractive. This can be understood in terms of direct electrostatic interaction between CH_3 and H. At the adatom, the H is located 2.53 Å outside the outermost Rh layer (0.69 Å more than the H-Rh bond in the FS), and its positive charge is expected to be little screened by the metal electrons [see Fig. 2(a')]. A rough estimate of the electrostatic interaction between the two fragments can be obtained by approximating C and the four H atoms with point charges, whose value is determined by Lowdin population analysis. An attraction ≈ 0.1 eV stronger at the adatom than at the terrace site is obtained in this way, a result consistent at least in sign with the observed lowering by 0.29 eV of $E_{\text{int}}^{\text{TS}}$.

As for the association barrier, Ref. 15 reports very small difference in the association barrier for step (0.59 eV) and terrace (0.65 eV) sites. The increased TS binding energy, more negative ΣE^{TS} , at the step is compensated by a similar change in the FS, ΣE^{FS} . Interaction between fragments plays a minor role in their case.

We also find that this association reaction is site insen-

sitive but again for somewhat different reasons. Our association barrier at the (111) terrace site is 0.42 eV while it is 0.39 eV on the adatom. The adatom/terrace differences in adsorption energy for the fragments at the TS and in the FS are -0.24 and -0.49 eV, respectively, favoring in both cases the lower coordination site as expected but not compensating each other exactly as the "late-TS reaction" argument would imply. Being the FS more stabilized at the adatom than the TS, the effect of adsorption energy differences (rightmost column in Table I) is to increase the barrier for the association reaction at the lower coordination site. Nearly complete compensation is obtained only when the already mentioned site-dependent fragment interaction energy at the TS is included. Site insensitivity in the association barrier results therefore from a cancellation of different contributions. Whether such cancellation is accidental or might have deeper origin is not clear to us. Fragment interaction energy in the FS, included in our result and neglected in Ref. 15, explains the discrepancy in the reported numerical values for the terrace site but plays no role in determining site sensitivity of this reaction.

B. $\text{OH} \rightleftharpoons \text{O} + \text{H}$

According to our calculations, reaction-site sensitivity of OH dissociation and O+H recombination is opposite to proposed general rules. The dissociation is site insensitive (with 0.99 and 1.03 eV activation energies for terrace and adatom sites, respectively) while association reaction is site sensitive (with 0.96 and 0.66 eV barriers).

As for dissociation, its insensitivity comes again from cancellation of two distinct effects. On one hand, OH is strongly adsorbed to the terrace site (-2.88 eV) and selectively binds to adatoms (-3.20 eV). This term was not considered in Ref. 15, but we notice that using Eq. (6) instead of Eq. (7) would incorrectly result in negative activation barriers. On the other hand, the fragment interaction energy at the TS, $E_{\text{int}}^{\text{TS}}$, decreases from 0.52 to 0.18 eV going from the terrace to the adatom, compensating the IS binding energy change. Binding energies of O and H at the TS are instead quite insensitive to the substrate change: ΣE^{TS} is -7.17/-7.11 eV for terrace/adatom site.

Association is site sensitive ($E_{\text{act}}^{\text{ass}}=0.96/0.66$ eV on terrace/adatom). Final state contributions, $\Sigma E^{\text{FS}}+E_{\text{int}}^{\text{FS}}$, and ΣE^{TS} have little effect on the activation energy, and the difference of 0.30 eV is mainly due to TS interaction energy, $E_{\text{int}}^{\text{TS}}$, which is strongly reduced at the adatom. Let us now see the origin of this reduction. As for direct interaction, O–H distance is larger at the adatom (1.55 versus 1.39 Å), thus Pauli repulsion is lower in this case. As for bond sharing, one can notice that in adatom case [Fig. 2(b')] O and H share less Rh atoms than on clean surface [Fig. 2(b)]. Moreover, an electrostatic contribution, mediated by the surface, is to be expected: Oxygen attracts electrons from surrounding Rh atoms, which are then positively charged and repel H atom (at the TS, H is also slightly positive, according to Lowdin population analysis). On the perfect surface [see Fig. 2(b)], O is close to a hollow site and H is close to a neighboring one, disturbed by the two Rh atoms in between which acquire a positive charge of 0.16e each. On Rh/Rh(111) the situation is more favorable [Fig. 2(b')]: the oxygen atom sits in a bridge position between the adatom and a surface atom. These two atoms become positive by 0.22e and 0.16e, respectively, but H has to overcome the repulsion of the second one only before meeting O; as a result, the substrate-mediated interaction between O and H is much lower. This analysis also explains why our search for a TS with H close to the positively charged adatom was unsuccessful.

C. $\text{CH}_3\text{O} \rightleftharpoons \text{CH}_3 + \text{O}$

Dissociation of CH_3O into CH_3 and O is site insensitive ($E_{\text{act}}^{\text{diss}}=1.53/1.60$ eV for terrace/adatom site), the reason being the similar preferential adsorption to the adatom of both CH_3 in TS and CH_3O in the IS. Notice that if Eq. (6) were used instead of Eq. (7), the activation energy would be site sensitive but negative. The former expression thus appears of little use in the case of strongly adsorbed IS. The TS interaction term does not play a significant role ($E_{\text{int}}^{\text{TS}}=0.61/0.71$ eV for terrace/adatom). The association is also site insensitive ($E_{\text{act}}^{\text{ass}}=1.57/1.56$ eV), in agreement with the general analysis: both $\Sigma E^{\text{TS}}-\Sigma E^{\text{FS}}$ and $E_{\text{int}}^{\text{TS}}$ have little effect.

D. $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O} + \text{H}$

Methanol dissociation to CH_3O and H is surface sensitive ($E_{\text{act}}^{\text{diss}}=0.97/0.79$ eV), in agreement with the general rules discussed above. The change in barrier height is mostly due to a change in the adsorption energies of CH_3O and H at the TS, whose sum decreases (they become more bound) by 0.65 eV going from the terrace to the adatom. This is only partly compensated by the increases of methanol-substrate bond and of the TS interaction energy. The latter determines the surface sensitivity of the association reaction. Notice that in this case, somehow at variance with the general feeling that defect sites should enhance reactivity, the barrier increases from 0.89 to 1.08 eV going from the terrace to the adatom site due to the strong increase (from 0.29 to 0.55 eV) in the $E_{\text{int}}^{\text{TS}}$. To explain qualitatively this unusual behavior we can again resort to some electrostatic argument combined with Lowdin population analysis of the fragments: CH_3O is negatively charged and has withdrawn electrons from the

closest Rh atom which becomes slightly positive. On the perfect surface [see Fig. 2(d)], this atom is farther than CH_3O from the approaching H atom, whereas on Rh/Rh(111) [see Fig. 2(d')] the positively charged Rh is the adatom itself, which strongly repels H.

E. $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3 + \text{OH}$

In agreement with the argument presented in Ref. 15, dissociation of CH_3OH to CH_3 and OH is sensitive to the change of reaction site (1.84/1.06 eV for terrace/adatom). As expected from the general analysis, the major contribution to the sensitivity is the change of ΣE^{TS} (−3.24/−4.35 eV). Also for the association barrier there is good agreement with the general analysis being much less sensitive than the dissociation barrier (1.80/1.65 eV). When going from the perfect surface to the adatom, the changes in $\Sigma E^{\text{TS}}-\Sigma E^{\text{FS}}$ and E_{int} are both small with respect to the large activation energy and partly compensate each other.

We now summarize the above discussion and compare with the arguments of Ref. 15, in order to extend these considerations. Three out of five of the dissociation reactions considered here are site sensitive as expected. These are the reactions where the associated molecules [CH_4 in (a) and CH_3OH in (d) and (e)] are weakly bound to the surface. The other two dissociation reactions (OH and CH_3O) are site insensitive because the adsorption energy of the reactant is comparable to the one of the products, and similarly site dependent. Therefore in general, $E_{\text{AB}}^{\text{IS}}$ should not be neglected and, when large, can reduce site sensitivity. For association reactions, we generally found an approximate compensation in the changes of TS and FS adsorption energies, ΣE^{TS} and ΣE^{FS} . Their contribution to the activation energy (rightmost column in Table I) is slightly lower at the adatom, meaning that adsorption is stabilized by this geometry more in the TS than in the FS (the only reported exception is $\text{CH}_3+\text{H} \rightarrow \text{CH}_4$). The interaction term can then become the determining contribution. It does not necessarily lower the barrier when moving to defects and, for example, $\text{CH}_3\text{O}+\text{H} \rightarrow \text{CH}_3\text{OH}$ becomes less favorable at the adatom due to an increase of $E_{\text{int}}^{\text{TS}}$. In many cases substrate-mediated repulsion between fragments is fairly dependent on the reaction site and, in general, $E_{\text{int}}^{\text{TS}}$ should be taken carefully into account.

Before concluding, we remark that the above analysis did not cover all the reactions investigated, but only those for which the general rules presented above could be applied. $\text{CH}_4+\text{O} \rightleftharpoons \text{CH}_3+\text{OH}$, where H is exchanged between a methyl and an oxygen atom [Fig. 2(f)], is not a dissociation/association reaction. A detailed analysis would be out the scope of this paper since it is not relevant in determining the rate-limiting steps of methane-to-methanol conversion. We just mention that its activation energy is rather site insensitive due to large compensation between the cleavage of a “double” O-metal bond and the creation of two “single” CH_3 - and OH-metal bonds. The other reaction mentioned here is direct insertion of O in a C–H bond to form methanol, $\text{CH}_4+\text{O} \rightleftharpoons \text{CH}_3\text{OH}$. This is indeed an association reaction, but not of the late-TS kind and would require again a different analysis. Results for this reaction have not been dis-

cussed in detail due to its high activation energy, much larger than that for the competing CH_4 dehydrogenation.

Coming back to the main issue of this work, to assess the possibility of using Rh catalysts for direct methane-to-methanol conversion, we recall that the rate-limiting steps for these process on Rh(111) and Rh/Rh(111) are the association steps of reactions (d) and (e). According to previous analysis they are both *site insensitive* and we have seen that this is not due to occasional cancellation of contributions but to the compensation between changes in ΣE^{TS} and ΣE^{FS} , and the minor part taken by $E_{\text{int}}^{\text{TS}}$.

Even if the precise behavior of this last term is difficult to predict, in this case it is of the order of 0.5 eV, and it is very unlikely that its site dependence can lower the activation energy by more than a fraction of an eV. This is not sufficient to make methanol formation preferred to further deprotonation of methyl radical.

V. CONCLUSIONS

We have investigated direct methane-to-methanol conversion on Rh(111) surfaces and on Rh adatoms on Rh(111) that was shown recently¹² to selectively activate the first dehydrogenation step of methane hindering the second one. We analyzed the possible reaction pathways leading to methanol formation and determined by DFT simulations the corresponding activation energies. On both substrates, the rate-limiting step involves C–O bond formation, with the following difference: on Rh(111) the process would proceed via the combination of CH_3 and O to CH_3O ($E_{\text{act}}=1.57$ eV) which then binds an additional H; on Rh/Rh(111) it would be more convenient to first form OH and then to combine CH_3 and OH ($E_{\text{act}}=1.65$ eV). The corresponding activation energies are, however, too large as compared to the one for the dehydrogenation of CH_3 ($E_{\text{act}}=0.5$ eV) and CH_3OH cannot form. The adatom site, in particular, does not favor methane-to-methanol conversion.

By discussing the site sensitivity of the individual association/dissociation reactions in terms of recently proposed general rules¹⁵ it has been possible to show that these results are likely to extend to generic Rh surfaces, thus ruling out Rh as candidate catalyst for methanol synthesis.

ACKNOWLEDGMENTS

The authors would like to thank Nicola Bonini, Anton Kokalj, Stefano Baroni, Renzo Rosei, and Carlo Sbraccia for stimulating discussions. This work has been supported in part by the Italian MIUR through PRIN. Calculations were performed at the CINECA Computing Center. The authors also thank INFN for computing grants.

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