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Understanding the dual active sites of FeO/Pt(111) interface and reaction kinetics: A density functional theory study on methanol oxidation to formaldehyde

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Abstract

Identifying the active sites and reaction kinetics for a catalytic reaction can provide significant insight to the catalytic systems. By conducting DFT calculations, the catalytic activity of FeO/Pt(111) interfacial sites, which is an important class of catalyst with excellent activity, for methanol partial oxidation is carefully examined and compared. The O-H cleavage barrier of methanol is significantly diminished to below 0.1 eV with the aid of interfacial oxygen, which is much lower than that on the Pt(111) surface (> 0.8 eV). The CH_3O^* intermediate can further undergo a C-H bond breaking process to produce formaldehyde via a low barrier (~ 0.2 eV) at the interfacial Pt sites. Assisted by interfacial Pt-O ensemble, the O-H and C-H bond cleavage are greatly facilitated, suggesting that the FeO/Pt bi-phase system could effectively combine the advantages of two individual phases. To investigate the rate determining steps, a multi-site

micro-kinetic model is applied at FeO/Pt interface. The results show that the overall rate can be significantly improved by lower the activation energy of interfacial oxygen removal steps. Interestingly, the turnover frequency (TOF) can also be enlarged when increasing the barriers of O₂ dissociative adsorption on the Pt flat surface, which is a special feature in multi-phase systems comparing with the mono-phase one. The active site and micro-kinetic studies in our work can provide insights into the development of metal/oxide catalysts for the partial oxidation of methanol or other primary alcohols.

Key words: Density functional theory, FeO/Pt interface, methanol partial oxidation, multi-sites micro-kinetic model, turnover frequency

1. Introduction

The oxide-supported transition metal catalysts (TM/MO_x) have been widely used in industrial applications, such as oxide-supported Ag catalysts for ethylene epoxidation¹⁻² and CeO₂-supported materials in the automotive three-way catalysts (TWC) for emission control.³⁻⁵ Generally, the catalytic activities can be considerably enhanced by the dispersion of metal particles into oxide supports, ascribing to the increase of specific surface area and active sites⁶ and perhaps the electronic property change of both oxide and metal constituents. Recently, this kind of bi-phase catalytic systems have gained growing attentions.⁷⁻⁸ To elucidate the related reaction mechanism on TM/MO_x-based catalysts, most theoretical work focuses on the study of the mono-phase constituent, in which the catalytic role of metal or oxide has been comprehensively addressed.⁹ Taking Ag/ α -Al₂O₃ for ethylene epoxidation as an example, by simply conducting theoretical investigation on silver surface, the reaction mechanism could be acquired and the theoretical work is in well agreement with experimental results, owing to the α -Al₂O₃ acting as an inert support to disperse Ag particles. In addition, the properties of oxide supports have also been extensively investigated. For example, for TWC catalysts, the CeO₂ support is regarded as an indispensable component, in which the superb oxygen storage and release properties of ceria oxide have been critically addressed.

The studies of mono-phase component could indeed give significant insight into certain

catalytic processes; however, some recent work indicates that the neglected interfacial sites play a crucial role in the catalytic activity boost in some oxide/metal bi-phase systems.¹⁰⁻¹³ For example, Shaikhutdinov and co-workers reported that the iron oxide film on Pt(111) can promote low temperature CO oxidation.¹⁰ Furthermore, Bao and co-workers discovered that the exposed ferrous centers at the interface are important active sites contributing to the enhancement of catalytic oxidation on the FeO/Pt catalysts.¹¹ By fabricating a series of metal/oxide systems, including several Pt, Pd and Ag supported transition metal oxide (Fe, Co, Ni, Cu, Mn, *et al*) and their reversed systems, Li and co-workers discovered that the interfacial sites are highly active and should be responsible for the activity enhancement of benzyl alcohol partial oxidation.¹⁴ In such systems, by simply investigating the mono-phase constituent, the promotion effects of interfacial sites might be ignored, resulting in misunderstandings of real catalytic processes. However, the complexity and diversity of interfacial sites largely hindered the study of reaction mechanisms and kinetics.

Recently, a number of ultrathin oxide film-covered metal systems, the so-called inverse model catalysts, have been extensively synthesized and investigated,¹⁵⁻¹⁷ such as MO_x (M= Fe, Mn, Ti, Zr) on Pt(111),¹⁸⁻²⁵ MnO_x, CoO_x and NiO_x on Pd(100),²⁶⁻²⁹ TiO_x and VO_x on Au(111) surface.³⁰⁻³¹ The sophisticated bi-phase images could thus be observed by the microscope technologies, which provide valuable information on the interfacial configuration of the metal/oxide systems. Furthermore, by virtue of density functional theory (DFT) calculations, the electronic properties of interface could be characterized and the reaction mechanism at active sites could be identified, which help us obtain a clear picture of how the interfaces work on catalytic reactions in metal/oxide bi-phase systems. Among the systems of metal-supported ultrathin films, the Pt-supported iron oxide film (FeO/Pt) has been widely studied.^{10, 18, 32-34} Using high-resolution scanning tunneling microscopy (STM), Wendt and co-workers uncovered the active sites and boundary structures of pristine, oxidized and reduced FeO islands on Pt(111) at atomic-scale.³³⁻³⁴ Theoretically, the magnetic and electronic properties of FeO/Pt(111) are characterized by Giordano and co-workers.¹⁹ They also compared the results obtained from PBE+U and HSE06 approaches and showed that the DFT+U approximation

remains an adequate tool for the studies of the similar metal-supported ultrathin oxide film systems.³⁵ Moreover, Li and co-workers investigated the reaction mechanism of CO oxidation at the FeO/Pt(111) interface; they found that the oxygen can be readily dissociated at these sites, and the OH group can further facilitate the oxygen activation and CO oxidation.^{11, 32}

Although a great progress has been achieved in the study of metal/oxide systems, many reaction mechanisms and kinetics are still inadequately addressed at the interfacial sites of bi-phase systems. In order to fully understand the catalytic role of interfacial sites, one must answer the following two questions: (i) what is the role of each component in multi-phase systems? (ii) how do the interfacial sites affect the overall reaction kinetics? To provide insight into the metal/oxide systems and address the questions mentioned above, a detailed investigation was carried out on the FeO ribbon supported Pt(111) (FeO/Pt) bi-phase system by using methanol partial oxidation ($\text{CH}_3\text{OH} + 1/2 \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$) as a model reaction. The reasons for the selected system are described as follows: Firstly, the Pt(111)-supported FeO film can be regarded as a simplified model of reverse oxide-supported metal catalyst, which is among the most studied transition metal-supported ultrathin film systems.^{10, 32-34} The unambiguous interfacial structure can be constructed on account of the extensively previous studies on the FeO/Pt system by STM and DFT calculations.³³⁻³⁴ Secondly, the theoretical studies of oxidation reactions were limited on FeO/Pt and other oxide/metal interfaces. The investigation of alcohol partial oxidation to aldehyde may provide insight into the general rules of oxidation reactions on the oxide/metal bi-phase systems. Thirdly, as the simplest analogues of alcohol, methanol is an ideal model molecule to examine the alcohol partial oxidation process at the bi-phase interface. In addition, formaldehyde is an important product in the methanol decomposition process,³⁶⁻³⁸ which is also an extensively used chemical in industries of adhesives and plastics production.³⁹ In the present work, the overall reaction profiles are plotted and compared at different sites of the FeO/Pt system, in which the thermodynamically favorable pathway and the active species have been identified. The crucial elementary steps of methanol partial oxidation, including formaldehyde and water formation, are determined and elucidated in a multi-site micro-kinetic framework,⁴⁰⁻⁴² with the rate control steps and the role of interfacial

sites revealed and discussed. The results would provide insight into the design of metal/oxygen systems for the partial oxidation of methanol and other primary alcohols.

2. Methods and Models

2.1 Methods

The spin-polarised calculations were performed with the Perdew-Burke-Ernzerhof (PBE)⁴³ functional within the generalised gradient approximation (GGA) as implemented in the Vienna Ab initio Simulation Package (VASP).⁴⁴⁻⁴⁵ The project-augmented wave (PAW) method was used to represent the core-valence electron interaction.⁴⁶⁻⁴⁷ The valence electronic states were expanded in plane wave basis sets with a cutoff energy of 450 eV. To accurately treat the electron of transition metal oxides, the on-site column repulsion was described for FeO/Pt bi-phase systems by DFT+U approach⁴⁸⁻⁴⁹ with $U - J = 3$ eV for Fe 3d orbitals, as used in previous studies.^{11, 35, 50} To model the methanol partial oxidation on metal mono-phase, a four-layer $p(3 \times 3)$ Pt(111) slab (Fig. S1) was used (9 Pt atoms in each layer) with $4 \times 4 \times 1$ k -point sampling. For FeO/Pt interface simulations, a FeO ribbon covered $(2\sqrt{3} \times 5)$ Pt(111) slab model was applied with $3 \times 2 \times 1$ k -point sampling. The FeO ribbon consists of three Fe and three O columns with Fe atoms coordinated with the top layer of Pt substrate (Fig. 1a). To balance the computational cost and accuracy, a three-layer Pt(111) metal substrate was used (20 Pt atoms in each layer). The bottom two layers of the Pt substrates were fixed, and the other atoms were all relaxed during the structural optimization. A vacuum layer of 15 Å for all calculated models was applied along the z direction to avoid the interactions between periodically repeated slabs. The atomic positions were optimized using the Broyden-Fletcher-Goldfarb-Shanno minimization scheme until the maximum force of each atom was less than 0.05 eV/Å.

Reaction pathways were searched with a constrained minimization technique.⁵¹⁻⁵³ In this approach, we constrain the distance between the reactants in each elementary step and minimize the total energy with respect to all remaining degrees of freedom. This method allows the transition complex to rotate and translate subject to the above constraint. The transition state is verified when (i) all forces on the atoms vanish; and (ii) the total energy is a maximum along

the reaction coordinate but a minimum with respect to the rest of the degrees of freedom. The vibration frequency calculations were tested for the transition state (TS) structures, which show that the TS structures we located are true saddle points. The adsorption energy of species X ($E_{ad}(X)$) is defined as (Eq 1),

$$E_{ad}(X) = E_{X/surf} - E_X - E_{surf} \quad (\text{Eq 1})$$

in which E_X , E_{surf} , $E_{X/surf}$ are the total energies of adsorbates X in the gas phase, the clean surface and the optimized adsorbates/surface system, respectively. Thus, a more negative value of $E_{ad}(X)$ corresponds to a stronger adsorption of species X on the surface. The activation energy (E_a) is determined by the energy difference between the transition state and initial state in each corresponding elementary step.

2.2 Models

The metal/oxide interfacial structures of reduced and oxidized FeO islands on Pt(111) are illustrated in Fig. 1. For the reduced FeO/Pt structure, the FeO/Pt interface is terminated with Fe atoms (Fe-FeO/Pt, Fig. 1a), which can act as the active binding sites. The coordinatively unsaturated ferrous site (CUF) shows a strong oxygen binding ability (-1.28 eV heat release) and can readily be oxidized via a low oxygen dissociation barrier (0.34 eV), with O-O bond length elongation to 1.77 Å in the transition state (Fig. 1b) from 1.43 Å in the O₂* adsorption state, which is consistent with the previous work of Bao and co-workers who gave an activation energy of 0.42 eV at the PW91 functional level.¹¹ After oxygen dissociation, the exposed Fe sites are saturated by adsorbed oxygen, resulting in the O-terminated FeO/Pt interface (O_{2c}-FeO/Pt, Fig. 1c). The O_{2c} atom, coordinated with boundary Fe and substrate Pt, can further migrate to the bridge site of Fe atoms, leading to the 3-fold coordinated oxygen formation (O_{3c}-FeO/Pt, Fig. 1d).³³⁻³⁴ It is worth noting that, the total energy difference of the O_{3c}-FeO/Pt and O_{2c}-FeO/Pt structure is only 0.02 eV thermodynamically, indicating the two structures can both exist. As can be seen in Fig. 1, another O-terminated FeO/Pt interface also exists at the other side of FeO ribbon, in which oxygen atoms are located at the bridge site of marginal Fe atoms without bonding with substrate Pt atoms (denotes as O_{bri}-FeO/Pt, Fig. 1d, e). According to

previous work by Wendt and co-workers,³³⁻³⁴ the FeO/Pt interface can undergo the transformation from Fe-FeO/Pt into the O_{3c}-FeO/Pt structure and further to the stable O_{bri}-FeO/Pt boundary (Fig. 1e) during the oxygenation process. Thus, both the Fe- and O-terminated FeO/Pt interfaces (O_{2c}-FeO/Pt, O_{3c}-FeO/Pt and O_{bri}-FeO/Pt) are considered in our study.

3. Results and Discussion

3.1 Methanol adsorption

To compare the binding abilities of methanol at interfacial sites, the methanol adsorption energies were calculated at a variety of sites of FeO/Pt interface, including the Pt and Fe sites at O- and Fe-terminated FeO/Pt interfaces. The detailed configurations of methanol adsorption are illustrated in Fig. 2. At the Fe- FeO/Pt interface, the CUF sites (Fig. 2a) are the primary binding positions for methanol adsorption, which gives an energy release of 0.70 eV. By contrast, the Pt sites show a weaker binding strength with methanol (-0.21 eV, Fig. 2b), close to the result obtained on Pt(111) (-0.23 eV). Under oxygen-rich conditions, the CUF sites can be readily oxidized, leading to the formation of O-terminated FeO/Pt interface, owing to a low activation barrier (0.36 eV) for the dissociation of oxygen.

On O_{2c}-FeO/Pt interface (Fig. 2c), the methanol adsorption is exothermic by 0.61 eV at the Fe site, showing no obvious difference from the CUF site (-0.70 eV). Surprisingly, the methanol adsorption is dramatically enhanced (-0.76 eV) at the Pt site of O_{2c}-FeO/Pt (Fig. 2d), stronger by over 0.5 eV than those at the same sites of Fe-FeO/Pt and Pt(111) surfaces. The result shows that the interfacial Pt and O atoms (denote as Pt-O ensemble) can synergistically promote the methanol adsorption by providing adsorbed sites and forming hydrogen bond with methanol. Similarly, the Pt-O ensemble of O_{3c}-FeO/Pt interface is also highly active for methanol adsorption (0.83 eV exothermic), with a hydrogen bond formed and the interfacial oxygen moved away from the Fe-Fe bridge site (Fig. 2e). The other side of O_{3c}-FeO ribbon, terminated by bridge oxygen O_{bri} (O_{bri}-FeO/Pt, Fig. 2f), was evaluated for the methanol adsorption. The binding strength of methanol is still high (-0.89 eV, Table S3) at the Pt-O ensemble of O_{bri}-FeO/Pt interface, showing the interfacial Pt-O ensemble could indeed improve the methanol

adsorption in comparison with the mono-phase Pt sites.

The methanol adsorption energies at the above sites are plotted in Fig. 2g, which shows the binding strength of methanol can be greatly enhanced at the Pt-O ensembles of O-FeO/Pt interfaces. It can be ascribed to the formation of strong hydrogen bond between interfacial oxygen and the hydrogen of hydroxyl in methanol. The weakest methanol binding strength is found on the Pt(111) surface while both the Fe- and O-terminated FeO/Pt interfaces could provide active sites (Fe or Pt atoms) for methanol adsorption. It indicates the methanol would be accumulated at the FeO/Pt interface under experimental condition, which is consistent with the previous results of alcohol analogues (benzyl alcohol) adsorption at FeO/Pt interface.¹⁴

3.2 Methanol decomposition at Fe-FeO/Pt interface

The reaction pathways of CH₃OH decomposition have been comprehensively investigated on platinum surfaces in previous studies.³⁶⁻³⁷ The formaldehyde formation can start with O-H bond scission to remove the first hydrogen, then followed by the C-H bond cleavage to remove the second hydrogen (pathway 1, Scheme 1). Alternatively, the C-H bond cleavage can firstly occur, leading to CH₂OH* intermediate formation; then the formaldehyde can be produced by the subsequent O-H bond dissociation of CH₂OH* species (pathway 2, Scheme 1).

In this work, DFT calculations were initially carried out at the Fe-FeO/Pt interface, where the CUF sites are highly active for methanol adsorption (-0.70 eV). In pathway 1, the first hydrogen stripping occurs through the transition state (TS1, Fig. 3b) with an O-H distance of 1.23 Å in methanol. The hydrogen can be transferred to a nearby 3-fold coordinated oxygen (O_{latt}) in the FeO ribbon, resulting in an O_{latt}-H distance of 1.22 Å in the TS. The O-H cleavage step is slightly endothermic by 0.15 eV via a 0.46 eV barrier, leading to the formation of O_{latt}H and methoxyl (CH₃O*) intermediates (IM, Fig. 3c) at Fe site. The second hydrogen cleavage is occurred by C-H bond breaking of CH₃O* species, in which the hydrogen can be transferred to another nearby O_{latt} via the TS2 (Fig. 3d). The C-H dissociation step is endothermic by 0.18 eV, while the activation barrier is much higher than that of O-H cleavage (1.16 vs. 0.46 eV), suggesting that the C-H breaking process could hardly proceed. In pathway 2, the hydrogen

transfers from carbon to O_{latt} as a start, in which the C-H bond is elongated to 1.54 Å in the transition state (TS1', Fig. 3e). The C-H bond breaking step is endothermic by 0.86 eV via a large activation energy (1.63 eV), suggesting that this process should be difficult to proceed. Then a hydrogen bond can be formed between another O_{latt} and the hydrogen of CH_2OH^* species (IM', Fig. 3f). The subsequent O-H bond cleavage of CH_2OH^* occurs by hydrogen transfer to O_{latt} via transition state TS2' (Fig. 3g). The O-H bond breaking is exothermic by 0.89 eV and undergoes a low activation energy (0.10 eV).

After formation of two $O_{\text{latt}}\text{H}$, the formaldehyde is produced and adsorbed at the Fe site via oxygen atom (Fig. 3h). The further desorption of formaldehyde is endothermic by 0.83 eV, leading to the formation of $O_{\text{latt}}\text{H}$ adsorbed FeO/Pt structure. One can see from Table 1 that the C-H bond cleavage apparently undergoes a much higher activation energy (over 1 eV) than O-H bond breaking (under 0.5 eV) in the above two pathways. Thus, at CUF site of the Fe-FeO/Pt interface, C-H bond dissociation should be the rate determining step for formaldehyde formation. Additionally, the overall activation energy of pathway 1 is lower than that of pathway 2, suggesting the former pathway is kinetically favored.

3.3 Methanol decomposition at O-FeO/Pt interface

The Fe-FeO/Pt interface could be oxidized and transformed to the O-terminated interface under experimental condition, as discussed in the model construction section. To uncover the catalytic activity of the oxidized FeO/Pt interface, detailed calculations were performed on the reaction pathways at the O_{2c} -FeO/Pt interface and other two relevant oxygen edges (O_{3c} - and O_{bri} -FeO/Pt interfaces). In pathway 1, the hydrogen is transferred from the oxygen of methanol to the interfacial oxygen (O_{2c}) via transition state TS1 (Fig. 4b). Remarkably, the activation barrier of O-H bond cleavage is diminished to 0.04 eV, indicating that the hydrogen transfer process can readily occur at the O_{2c} -FeO/Pt interface. The CH_3O^* intermediate (IM, Fig. 4c) adsorbs at a Pt site of O_{2c} -FeO/Pt, and then the CH_2O^* is formed via the C-H bond scission. In the transition state (TS2, Fig. 4d), the C-H bond of CH_3O^* is elongated to 1.38 Å, and then the hydrogen could transfer to another Pt site, which is similar to the case on the Pt(111) surface (Fig. S1e).

The C-H cleavage step is exothermic by 0.42 eV with a not high barrier (0.17 eV). The subsequent migration of dissociated hydrogen to interfacial oxygen will lead to an energy release by -0.79 eV. In pathway 2, the hydrogen atom transfers from carbon to Pt atom as a start, in which the C-H bond distance is elongated to 1.45 Å in the TS structure (TS1', Fig. 4e). The activation energy of C-H cleavage is 0.68 eV, close to the value at Pt(111) (0.67 eV). The possibility of C-H cleavage assisted by interfacial oxygen is also tested; however, its activation energy is higher than direct C-H bond breaking at Pt sites. The CH₂OH* intermediate adsorbs at two neighboring Pt atoms via C and O, and forms a hydrogen bond with an interfacial O_{2c} (IM', Fig. 4f). Subsequently, the hydrogen of hydroxyl could transfer to O_{2c} with a low activation energy (0.03 eV, Fig. 4g). An OH-terminated FeO/Pt interface (OH-FeO/Pt) would be gradually formed during the methanol decomposition and formaldehyde desorption process (0.30 eV endothermic). Notably, the interfacial hydroxyl should be removed to provide free sites for oxygen chemisorption and eventually restore the interfacial structure.

The O-H bond cleavage step was also investigated on the other two O-terminated FeO/Pt interfaces (O_{3c}-FeO/Pt and O_{bri}-FeO/Pt). For the O_{3c}-FeO/Pt interface (Fig. S3a~c), hydrogen bond could be formed between methanol and interfacial O_{3c}, which will make the O_{3c} atom move to the 2-fold coordinated site (like O_{2c}). Likewise, at the O_{bri}-FeO/Pt interface (Fig. S3d~f), a hydrogen bond could also be formed between methanol and interfacial oxygen (O_{bri}). Assisted by interfacial O_{3c} and O_{bri}, the O-H bond cleavage of methanol would be readily proceeded via a very low barrier (below 0.1 eV), which is in consistent with the results obtained at the O_{2c}-FeO/Pt interface. The result suggests that the interfacial oxygen of the FeO/Pt interface could generally act as an active site for the stripping of hydrogen from the hydroxyl of methanol, which is well consistent with our previous work that the O-H bond of benzyl alcohol is effectively activated by the interfacial oxygen of FeO/Pt interface.¹⁴

As the formaldehyde formation proceeds, the O-FeO/Pt interface will be gradually transformed to OH-terminated FeO/Pt boundary. It is notable that the hydroxyl removal would be hindered if the OH binding strength is too strong at the interfacial sites, which will block the overall catalytic cycle. For simplicity, the energy of oxygen vacancy (O_v) formation ($\text{O}^* \rightarrow 1/2 \text{O}_2 + *$)

was calculated in order to estimate the binding strength of hydroxyl species. Generally, a higher E_{O_v} (stronger O^* binding) suggests a more difficult O^* removal process ($O^* \rightarrow 1/2 O_2$ or $O^* + H_2 \rightarrow H_2O + *$).⁵⁴⁻⁵⁶ At the O_{2c} - and O_{3c} -FeO/Pt interfaces, the O_v formation energies are only around 1 eV. However, the O_v formation is much more difficult at the O_{bri} -FeO/Pt interface (1.90 eV), suggesting that the further OH removal would be harder. The total energy of O_{2c} -FeO/Pt interface is lower than O_{3c} -FeO/Pt by 0.42 eV, ascribing to the formation of hydrogen bonds between the neighboring hydroxyl at the O_{2c} -FeO/Pt interface (Fig. S4). Thus, the O_{2c} -FeO/Pt interface is most likely to be formed under the reaction condition.

3.4 Activity comparison between interface and mono-phase sites

To compare the reaction activities of interface and mono-phase sites, we further carried out calculations on Pt(111). On the Pt(111) surface, the methanol decomposition can start with the O-H bond scission to remove the first hydrogen via an activation energy of 0.87 eV, and then the second hydrogen can be removed by the C-H bond activation via a 0.24 eV barrier with 0.34 eV heat releasing in pathway 1. Alternatively, the C-H bond cleavage can firstly occur via an activation energy of 0.67 eV, then followed by the O-H bond dissociation via a 0.81 eV reaction barrier in pathway 2. The reaction profiles are illustrated in Fig. 5. One can see that the reaction profile of pathway 2 is under that of pathway 1 on the Pt(111) surface, implying that the C-H bond breaking is preferred to start the methanol decomposition. Besides, the O-H cleavage step, having a much higher barrier (over 0.8 eV) than the C-H breaking step in both pathways, could be regarded as the main obstacle that prevents the methanol decomposition. In contrast, at the O-FeO/Pt interface, the interfacial oxygen species, including O_{2c} , O_{3c} and O_{bri} , show a stronger attraction of hydrogen and are all highly active for the hydrogen stripping from the hydroxyl of methanol, in which the activation energies of O-H bond breaking are remarkably reduced to below 0.1 eV with the aid of the interfacial oxygen. For the C-H bond cleavage, the kinetic barriers show little difference from those results obtained on the Pt(111) surface. One can see from the energy profile (Fig. 5) that the C-H bond breaking needs to overcome a higher barrier than the O-H bond cleavage in both pathways; and pathway 1, which starts with the O-H bond cleavage, should be a favorable pathway for methanol decomposition

at the O-FeO/Pt interface. Thus, by comparing the reaction profiles on the Pt(111) surface and O-FeO/Pt interface, the interfacial Pt-O ensemble obviously showing more advantage than mono-phase Pt sites in methanol decomposition.

Regarding FeO oxide, we could estimate its activity from the results at the Fe-FeO/Pt surface, because the local structure of FeO ribbon is close to the FeO(111) mono-layer, and the Pt sites were not involved in the calculation. Actually, the interfacial Fe sites of Fe-FeO/Pt should be more active than those of FeO(111), because the unsaturated Fe atom could provide an appropriate binding site for methanol adsorption. When the Fe atom is saturated by oxygen (Fig. 2c), the binding strength of methanol would be weakened in comparison with the CUF site (Fig. 2a). The O_{latt} of FeO ribbon, exhibiting similar local configuration of the oxygen on the FeO(111) surface, could also abstract the hydrogen of hydroxyl in methanol; however, the kinetic barriers are higher than those at the interfacial Pt-O ensemble. Furthermore, a much higher activation energy (over 1 eV, Table 1) is required for the C-H bond breaking, indicating that the overall reaction rate should be slower at Fe sites of FeO ribbon. It is also noteworthy that the removal of adsorbed $O_{\text{latt}}H$ on the FeO mono-phase is required to complete the catalytic cycle, which is difficult to proceed (~ 2.9 eV needed to form oxygen vacancies). Therefore, the FeO mono-phase, alike the FeO ribbon, is predicted to be inert for catalyzing the methanol decomposition. Clearly, the mono-phases of FeO or Pt could not effectively promote the reaction of methanol decomposition, while the interfacial Pt-O ensemble of FeO/Pt show a much better performance.

3.5 Formation of oxygen vacancy and water

To complete the catalytic cycle, the interfacial hydroxyl should be removed to provide free sites for subsequent oxygen adsorption and dissociation. To evaluate the hydroxyl coverage effect at the interfacial sites, calculations were carried out at the OH-terminated FeO/Pt interface for overall methanol partial oxidation. Pathway 1 was regarded as a more favorable route and its elementary steps were investigated in this part, considering the overall barrier in pathway 1 is lower than that in pathway 2 (over 0.6 eV). After the formaldehyde formation and desorption, the OH^* species can be removed with the aid of adsorbed hydrogen ($OH^* + H^* \rightarrow H_2O + 2^*$),

resulting in a water molecule desorption and an oxygen vacancy formation (denoted as O_v) at the FeO/Pt interface.

The reaction profile of the catalytic cycle is plotted with detailed structures depicted in Fig. 6, in which the reaction starts with oxygen adsorption (1.40 eV exothermic) at the interfacial free site (O_v). The methanol adsorption is exothermic by 0.55 eV at the OH-FeO/Pt interface with a 2/3 hydroxyl coverage. The binding strength of methanol is weaker at the OH-FeO/Pt interface than O-FeO/Pt interface by 0.21 eV, which is probably due to the fact that the formed hydrogen bond is weakened at the hydrogen-rich interface. The methanol decomposition starts with O-H scission, in which the O-H bond distance elongates to 1.34 Å in the transition state. Likewise, the O-H bond breaking barrier is not high (below 0.1 eV) in the aid of interfacial oxygen. In the subsequent step, the C-H bond scission of CH_3O^* gives an activation energy by 0.22 eV at the OH-FeO/Pt interface, close to the values at O_{2c} -FeO/Pt interface and Pt(111) (0.17, 0.24 eV, respectively). The dissociated hydrogen (H^*) can migrate to the FeO/Pt interface and attack the interfacial hydroxyl. Then an H_2O can be formed via an activation energy of 0.51 eV, leading to an oxygen vacancy formation after water desorption. It is worth mentioning that even though the transition state structures of O-H scission and H_2O formation at the OH-terminated interface are similar to those at the O-terminated interface, the activation energies increase at the OH-FeO/Pt interface since the hydrogen binding is weakened at these hydrogen-rich interfacial sites. From the plotted standard free energy profiles, one can see that the C-H bond cleavage and water formation steps are probably the rate determining steps due to their relative high activation energies in the whole reaction cycle.

3.6 Kinetic study of overall catalytic cycle

After obtaining the reaction and activation energies of the catalytic cycle, we are now in the position of considering the reaction kinetics of the FeO/Pt bi-phase system. Generally, the reaction scheme can be described as follows: O_2 and CH_3OH adsorb on the surface, and the adsorbed O_2^* dissociates into atomic O^* species. Then the CH_3OH^* decomposition occurs and leads to the formation of CH_2O ; and the adsorbed H^* combine with O^* to form H_2O^* . Finally,

the formed CH_2O^* and H_2O^* molecules desorb into the gas phase. The following approximation is taken in our kinetic model: The adsorption and desorption of O_2 is considered to be in equilibrium, which can be combined as $\text{O}_2 + 2^* \rightarrow 2\text{O}^*$ (X^* and * are defined as the adsorbed X species and a surface free site, respectively). Likewise, the reactions of $\text{CH}_3\text{O}^* + ^* \rightarrow \text{CH}_2\text{O}^* + \text{H}^*$ and $\text{CH}_2\text{O}^* \rightarrow \text{CH}_2\text{O} + ^*$ can be combined into $\text{CH}_3\text{O}^* \rightarrow \text{CH}_2\text{O} + \text{H}^*$; the $\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^* + ^*$ and $\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O} + ^*$ can be combined into $\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O} + 2^*$. The rate equation for each step is listed in Table S5, in which the rate constant of the forward (reverse) reaction can be derived from transition state theory⁵⁷, as shown in (Eq2).

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger,0}/k_B T} \quad (\text{Eq2})$$

Where k_B , h , and T represent the Boltzmann constant, Planck constant, and temperature in Kelvin. $\Delta G^{\ddagger,0}$ is the change of standard molar Gibbs free energy between the initial and transition state (i.e., energy barrier E_a). Moreover, to qualitatively determine the influence of single step to the overall reaction, the degree of rate control⁵⁸, defined in (Eq3), is calculated for each step.

$$X_{RC,i} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (\text{Eq3})$$

where the partial derivative of the rate constants, k_j , is hold constant, for all other steps $j \neq i$. Rate constants k_i and k_{-i} will be varied by equal factors so that their ratio remains constant. In other words, $X_{RC,i}$ measures the variance of the overall rate when slightly changing the energy of transition state of step i . Typically, $X_{RC,i}$ should be positive, which means that the overall reaction will decrease while increasing the energy of transition state of step i . Larger $X_{RC,i}$ value means a bigger influence of step i on the overall reaction, and the sum of all $X_{RC,i}$ should be unity.

A multi-site micro-kinetic model was employed in order to quantitatively determine the activity of the methanol partial oxidation at 500 K in our study (details see SI-14). Assuming that there are 10% interface sites (#1) and 90% Pt flat sites (#2), which is a quite reasonable assumption since the proportion of flat sites is normally larger than that of interfacial sites on the metal-

supported oxide systems. We also tested different ratios of #1/#2, showing no significant deviation on the kinetic trends. By testing and comparing the overall rates of pathway 1 and 2 (Table 2 and Table S10, respectively), we can confirmed that pathway 1 is much more favoured. In addition, we examined the performance of the catalyst when only Pt flat sites exist (i.e. without the FeO/Pt interface, Table S6), in which the activation energy of H₂O formation step is assumed to be zero for simplification. Some striking features can be obtained from the results of micro-kinetic modelling (Table 2, S7-S9). Firstly, we find that the exposed Fe sites of the interface are predominately covered by OH (9.97% out of 10%), which confirms the assumption of the interface will be an OH-terminated interface under the reaction condition. Secondly, one can see from the tables that the production rate of CH₂O at the FeO/Pt interface (3.57E-04, Table 2) is many orders of magnitude higher than that on Pt flat surface (1.56E-16, Table S8), indicating that the FeO/Pt interfaces indeed largely enhance the overall catalytic activity. Thirdly, the steps of $O_2(g) + 2_{\#2} \leftrightarrow 2O_{\#2}$ and $H_{\#2} + OH_{\#1} \leftrightarrow H_2O(g) + \#1 + \#2$ have the largest X_{RC} value in CH₃OH partial oxidation at the FeO/Pt (-2.00 and 1.99, respectively), suggesting that they influence the reaction most.

Interestingly, the X_{RC} of step $O_2(g) + 2_{\#2} \leftrightarrow 2O_{\#2}$ is negative, indicating that the overall reaction rate will be improved if increasing the energy barriers of O₂ dissociative adsorption at the Pt flat sites. Such a case (negative X_{RC}) may be a special feature of multi-site catalysis. Although O₂ dissociative adsorption has a lower energy barrier at the interface, the overall reaction network and site distribution make the interfacial oxygen primarily comes from O₂ dissociative adsorption at the Pt flat sites (#2) and surface diffusion (step 3 in Table 2), rather than directly dissociates at the FeO/Pt interfacial sites. In other words, the oxygen prefers to dissociate at the Pt flat sites kinetically. The CH₃OH*, CH₃O* and H* species have a much lower coverage than the O* species due to their large difference of binding energies at the Pt sites. Therefore, increasing the barrier of O₂ dissociative adsorption at the Pt sites will make the adsorption of other intermediates more pronounced and eventually facilitate the overall reaction. For example, the ratio of adsorbed CH₃OH* and turnover frequency (TOF) will both go up by two orders, provided that the barrier of O₂ dissociative adsorption increases by 0.25 eV.

Finally, it is worth mentioning some implications of the general guidelines on catalyst design of the metal/oxide interfaces for efficient methanol partial oxidation. Firstly, increasing the barrier of oxygen dissociative adsorption on metal surfaces can be effectively improving the overall TOF, which may be achieved by using other metal substrates. Inert metals can be potential candidates as the metal substrates, such as Ag and Au, which show a higher activation energy for oxygen dissociation⁵⁹⁻⁶¹ and have a similar methanol binding strength⁶² (~ -0.15 eV in our tests) on their low Miller index surfaces. Secondly, a suitable binding strength of O* species is of significance to balance the oxygen adsorption ($1/2 \text{ O}_2 + * \rightarrow \text{O}^*$) and its removal process ($\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O} + 2*$), which is also applicable in other oxidation reaction on oxide-based catalysts.⁶³⁻⁶⁴ It is clear that the O* binding strength at interface sites should be at least stronger than that at the sites of mono-phase constituent; otherwise, the interfacial O* will likely diffuse to the metal surface. On the contrary, too strong adsorption of O* will hinder the formation of oxygen vacancy and eventually block the overall catalytic cycle. Typically, the binding strength of interfacial O* species could possibly act as a descriptor for certain oxidation reaction in the metal/oxide bi-phase systems. Thirdly, the structural stability of metal/oxide interface is vital to guarantee its long-lasting work in practical operation. Although the thermal stabilities of different combination between oxide layers and support metals are not involved in our study, they can be evaluated by calculating the binding strength of MO_x on the support metal, which has been extensively studied by Plessow and co-workers.⁶⁵⁻⁶⁶

4. Conclusion

In summary, this work is aimed at obtaining a comprehensive understanding of interfacial effects on catalytic reactions. The methanol partial oxidation ($\text{CH}_3\text{OH} + 1/2 \text{ O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$) at the FeO/Pt interfaces was chosen as a model system to address in general how the interfacial sites promote a catalytic reaction. The methanol decomposition reaction on the Fe-FeO/Pt, O-FeO/Pt interfaces and Pt(111) surface was studied in detail, in which two possible pathways and reaction barriers were calculated. The results regarding adsorption energies of reactants and activation barriers are summarized in the following:

- (i) The methanol adsorption energy on the flat Pt(111) surface is only -0.23 eV, which is much weaker than the CUF site of Fe-FeO/Pt (-0.70 eV) and the Pt-O ensemble of O-FeO/Pt interfaces (-0.76 ~ -0.89 eV). The methanol binding strength at the Fe site (-0.61 eV) would be weakened when the exposed Fe atom is oxidized.
- (ii) At the Fe site of Fe-FeO/Pt interface, methanol decomposition requires to activate the O-H and C-H bonds via the activation energies of 0.46 and 1.16 eV, respectively, in pathway 1; while the reaction barriers of C-H and O-H bond breaking are 1.63 and 0.10 eV, respectively, in pathway2. Thus, at the Fe site of FeO ribbon, the activation energies of C-H bond cleavage (over 1 eV) are too high for the methanol decomposition in both pathways.
- (iii) On the Pt(111) surface, the O-H and C-H bond cleavage of methanol require to overcome the activation energies of 0.87 and 0.24 eV, respectively, in pathway 1; while the reaction barriers of C-H and O-H bond breaking are 0.67 and 0.81 eV, respectively, in pathway2. It is clear that the large barriers of O-H bond cleavage (over 0.8 eV) would hinder the methanol decomposition process at low temperatures.
- (iv) At the Pt-O ensemble of O_{2c}-FeO/Pt interface, the O-H and C-H bond cleavage of methanol require to overcome activation energies of 0.04 and 0.17 eV, respectively, in pathway 1; the reaction barriers of C-H and O-H bond breaking are 0.68 and 0.03 eV, respectively, in pathway2. Remarkably, in pathway 1, both steps of C-H and O-H bond cleavage could be facilitated via low activation barriers (below 0.2 eV), which could be rationalized that the C-H and O-H bond could be activated by interfacial Pt and O atoms, respectively.

By applying a multi-site micro-kinetic model, we obtain the following conclusions regarding the reaction process at the FeO/Pt interfaces:

- (i) The exposed Fe sites of the interface are predominately covered by OH* species, while the Pt substrate is mainly covered by O* species under the reaction condition. For the reactant adsorption, the methanol coverage is much higher at the FeO/Pt interface than the Pt(111) flat surface. The overall reaction rate of methanol partial oxidation at the FeO/Pt interface is dramatically faster than that on Pt mono-phase, showing significant advantages of

interfacial sites.

- (ii) The analyses of the degree of rate control X_{RC} suggest the oxygen dissociative adsorption ($O_2(g) + 2\#_2 \leftrightarrow 2O_{\#2}$) and its removal steps ($H_{\#2} + OH_{\#1} \leftrightarrow H_2O(g) + \#_1 + \#_2$) should be the rate determining step. Furthermore, it is notable that the former step shows a negative X_{RC} value, indicating the overall reaction will be faster when increasing the barriers of O_2 dissociative adsorption on the flat Pt substrate, which might be a special feature in multi-phase catalysis comparing to the mono-phase one.

Finally, based on the mechanistic and micro-kinetic studies on the FeO/Pt system, we arrive at some simple guidelines with respect to further improving the performance of metal/oxide catalysts as follows:

- (i) In metal/oxide systems, increasing the barrier of oxygen dissociative adsorption on the metal mono-phase by using other metal substrates, such as Ag and Au, may give rise to higher activity of methanol partial oxidation.
- (ii) Screening a better oxide/metal combination with suitable binding ability of interfacial oxygen species to balance the adsorption of oxygen and its removal process may be additionally beneficial to the systems.

Scheme 1 Methanol decomposition pathways on the surface of catalysts.

Fig. 1 Structures of FeO/Pt interfaces. (a) Fe-terminated FeO/Pt(111) interface with exposed CUF sites (Fe-FeO/Pt); (b) transition state structure of O₂ dissociation (O-O distance is 1.77 Å); (c) O_{2c}-terminated FeO/Pt(111) interface (O_{2c}-FeO/Pt); (d) O_{3c}- and O_{bri}-terminated FeO/Pt(111) interfaces (O_{3c}- and O_{bri}-FeO/Pt); (e) transformation of Fe-terminated edge to the most stable O_{bri}-terminated edge. Dark-blue balls represent for Pt atoms, purple for Fe and red for O. This notation is used throughout this paper.

Fig. 2 Methanol adsorption at different sites of FeO/Pt interfaces: (a) Fe site of Fe-FeO/Pt; (b) Pt site of Fe-FeO/Pt; (c) Fe site of O_{2c}-FeO/Pt; (d-f) Pt-O ensemble of O_{2c}-, O_{3c}- and O_{bri}-FeO/Pt interfaces, respectively; (g) bar chart of methanol adsorption energies at (a-f) sites and Pt(111). Grey balls represent for C and white for H. This notation is used throughout this paper.

Fig. 3 Optimized structures of CH_3OH decomposition on Fe-FeO/Pt interface: (a) CH_3OH adsorption; (b-d) TS of O-H cleavage (TS1), intermediate state (IM) and TS of C-H cleavage (TS2) in pathway 1; (e-g) TS of C-H cleavage (TS1'), intermediate state (IM') and TS of O-H cleavage (TS2') in pathway 2; (h) CH_2O adsorption.

Fig. 4 Optimized structures of CH₃OH decomposition on O_{2c}-FeO/Pt interface. (a) CH₃OH adsorption; (b-d) structures in pathway 1, including the TS of O-H cleavage (TS1), intermediate state (IM) and TS of C-H cleavage (TS2); (e-g) structures in pathway 2, including the TS of C-H cleavage (TS1'), intermediate state (IM') and TS of O-H cleavage (TS2'); (h) CH₂O adsorption.

Fig. 5 Reaction profiles of methanol decomposition at the Fe- and O_2c -FeO/Pt interfaces and flat Pt(111) surface. In the final state, the formaldehyde desorbs to the gas phase, and the dissociated hydrogen adsorbs at the interfacial oxygen site of FeO/Pt interface or the Pt site of Pt(111). The P1, P2 denote the pathway 1 and 2, respectively.

Fig. 6 The standard free energy profiles of methanol partial oxidation at the OH-FeO/Pt interface. The entropy effects of gas-phase O_2 , CH_3OH , CH_2O and H_2O are included ($T = 500$ K, the red line), in which $\Delta\mu_1 = \frac{1}{2}T\Delta S_{\text{O}_2} = 0.55$ eV; $\Delta\mu_2 = T\Delta S_{\text{CH}_3\text{OH}} = 1.37$ eV; $\Delta\mu_3 = T\Delta S_{\text{CH}_2\text{O}} = 1.27$ eV; $\Delta\mu_4 = T\Delta S_{\text{H}_2\text{O}} = 1.07$ eV. The insets depict the detailed structures of the related state.

Table 1 Reaction energies of methanol decomposition at the FeO/Pt interface and Pt(111) surface. The unit is eV.

Reactions	Fe-FeO/Pt		O-FeO/Pt		Pt(111)	
	E_a	ΔE	E_a	ΔE	E_a	ΔE
$\text{CH}_3\text{OH} + * \rightarrow \text{CH}_3\text{OH}^*$	N/A	-0.70	N/A	-0.76	N/A	-0.23
Pathway 1						
$\text{CH}_3\text{OH}^* + * \rightarrow \text{CH}_3\text{O}^* + \text{H}^*$	0.46	0.15	0.04	-0.02	0.87	0.64
$\text{CH}_3\text{O}^* + * \rightarrow \text{CH}_2\text{O}^* + \text{H}^*$	1.16	-0.18	0.17	-1.22	0.24	-0.34
Pathway 2						
$\text{CH}_3\text{OH}^* + * \rightarrow \text{CH}_2\text{OH}^* + \text{H}^*$	1.63	0.86	0.68	-1.13	0.67	-0.18
$\text{CH}_2\text{OH}^* + * \rightarrow \text{CH}_2\text{O}^* + \text{H}^*$	0.10	-0.89	0.03	-0.11	0.81	0.49
$\text{CH}_2\text{O}^* \rightarrow \text{CH}_2\text{O} + *$	N/A	0.83	N/A	0.30	N/A	0.37

Table 2 Forward (r_f), backward (r_b), overall (r) reaction rates and degree of rate control (X_{RC}) of each step of CH₃OH partial oxidation at the OH-FeO/Pt interface.

Reactions	r_f	r_b	r	X_{RC}
$O_2(g) + 2_{\#1} \leftrightarrow 2O_{\#1}$	2.00E-09	1.02E-13	2.00E-09	9.99E-01
$O_2(g) + 2_{\#2} \leftrightarrow 2O_{\#2}$	1.79E-04	9.12E-09	1.79E-04	-2.00E+00
$O_{\#2} +_{\#1} \leftrightarrow O_{\#1} +_{\#2}$	1.94E+03	1.94E+03	3.57E-04	-3.69E-07
$CH_3OH(g) +_{\#2} \leftrightarrow CH_3OH_{\#2}$	2.77E+01	2.77E+01	3.57E-04	8.79E-08
$CH_3OH_{\#2} + O_{\#1} \leftrightarrow CH_3O_{\#2} + OH_{\#1}$	1.27E-03	9.18E-04	3.57E-04	1.91E-03
$CH_3O_{\#2} \leftrightarrow CH_2O(g) + H_{\#2}$	3.57E-04	1.92E-14	3.57E-04	4.90E-03
$H_{\#2} + OH_{\#1} \leftrightarrow H_2O(g) +_{\#1} +_{\#2}$	3.57E-04	6.37E-10	3.57E-04	1.99E+00

Supporting information

The Supporting Information is available free of charge on the ACS Publications website:

- Additional tables and geometrical structures referred to in the main text.
- Additional micro-kinetic details referred to in the main text.

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References

- (1) Sachtler, W. M. H.; Backx, C.; Van Santen, R. A. *Catal. Rev.* **1981**, *23*, 127-149.
- (2) Minahan, D. M.; Hoflund, G. B. *J. Catal.* **1996**, *158*, 109-115.
- (3) Trovarelli, A. *Catal. Rev.* **1996**, *38*, 439-520.
- (4) Kašpar, J.; Fornasiero, P.; Graziani, M. *Catal. Today* **1999**, *50*, 285-298.
- (5) Jin, G.; Lu, G.; Guo, Y.; Guo, Y.; Wang, J.; Kong, W.; Liu, X. *J. Mol. Catal. A: Chem.* **2005**, *232*, 165-172.
- (6) Gates, B. C. *Chem. Rev.* **1995**, *95*, 511-522.
- (7) Chen, G.; Zhao, Y.; Fu, G.; Duchesne, P. N.; Gu, L.; Zheng, Y.; Weng, X.; Chen, M.; Zhang, P.; Pao, C.-W.; Lee, J.-F.; Zheng, N. *Science* **2014**, *344*, 495-499.
- (8) Kattel, S.; Yan, B.; Yang, Y.; Chen, J. G.; Liu, P. *J. Am. Chem. Soc.* **2016**, *138*, 12440-12450.
- (9) Mao, Y.; Chen, J.; Wang, H.; Hu, P. *Chin. J. Catal.* **2015**, *36*, 1596-1605.
- (10) Sun, Y. N.; Qin, Z. H.; Lewandowski, M.; Carrasco, E.; Sterrer, M.; Shaikhutdinov, S.; Freund, H. J. *J. Catal.* **2009**, *266*, 359-368.
- (11) Fu, Q.; Li, W.-X.; Yao, Y.; Liu, H.; Su, H.-Y.; Ma, D.; Gu, X.-K.; Chen, L.; Wang, Z.; Zhang, H.; Wang, B.; Bao, X. *Science* **2010**, *328*, 1141-1144.
- (12) Wang, Z.; Wang, H.-F.; Hu, P. *Chem. Sci.* **2015**, *6*, 5703-5711.

- (13) Meira, D. M.; Ribeiro, R. U.; Mathon, O.; Pascarelli, S.; Bueno, J. M. C.; Zanchet, D. *Appl. Catal., B* **2016**, *197*, 73-85.
- (14) Zhao, G.; Yang, F.; Chen, Z.; Liu, Q.; Ji, Y.; Zhang, Y.; Niu, Z.; Mao, J.; Bao, X.; Hu, P.; Li, Y. *Nat. Commun.* **2017**, *8*, 14039.
- (15) Rodriguez, J. A.; Ma, S.; Liu, P.; Hrbek, J.; Evans, J.; Pérez, M. *Science* **2007**, *318*, 1757-1760.
- (16) Suchorski, Y.; Wrobel, R.; Becker, S.; Weiss, H. *J. Phys. Chem. C* **2008**, *112*, 20012-20017.
- (17) Freund, H.-J.; Pacchioni, G. *Chem. Soc. Rev.* **2008**, *37*, 2224-2242.
- (18) Ritter, M.; Ranke, W.; Weiss, W. *Phys. Rev. B* **1998**, *57*, 7240-7251.
- (19) Giordano, L.; Pacchioni, G.; Goniakowski, J.; Nilius, N.; Rienks, E. D. L.; Freund, H.-J. *Phys. Rev. B* **2007**, *76*, 075416.
- (20) Hagendorf, C.; Sachert, S.; Bochmann, B.; Kostov, K.; Widdra, W. *Phys. Rev. B* **2008**, *77*, 075406.
- (21) Sachert, S.; Polzin, S.; Kostov, K.; Widdra, W. *Phys. Rev. B* **2010**, *81*, 195424.
- (22) Sedona, F.; Rizzi, G. A.; Agnoli, S.; Llabrés i Xamena, F. X.; Papageorgiou, A.; Ostermann, D.; Sambi, M.; Finetti, P.; Schierbaum, K.; Granozzi, G. *J. Phys. Chem. B* **2005**, *109*, 24411-24426.
- (23) Barcaro, G.; Agnoli, S.; Sedona, F.; Rizzi, G. A.; Fortunelli, A.; Granozzi, G. *J. Phys. Chem. C* **2009**, *113*, 5721-5729.
- (24) Meinel, K.; Eichler, A.; Schindler, K. M.; Neddermeyer, H. *Surf. Sci.* **2004**, *562*, 204-218.
- (25) Meinel, K.; Eichler, A.; Förster, S.; Schindler, K. M.; Neddermeyer, H.; Widdra, W. *Phys. Rev. B* **2006**, *74*, 235444.
- (26) Allegretti, F.; Franchini, C.; Bayer, V.; Leitner, M.; Parteder, G.; Xu, B.; Fleming, A.; Ramsey, M. G.; Podloucky, R.; Surnev, S.; Netzer, F. P. *Phys. Rev. B* **2007**, *75*, 224120.
- (27) Franchini, C.; Podloucky, R.; Allegretti, F.; Li, F.; Parteder, G.; Surnev, S.; Netzer, F. P. *Phys. Rev. B* **2009**, *79*, 035420.

- (28) Allegretti, F.; Parteder, G.; Gragnaniello, L.; Surnev, S.; Netzer, F. P.; Barolo, A.; Agnoli, S.; Granozzi, G.; Franchini, C.; Podlousky, R. *Surf. Sci.* **2010**, *604*, 529-534.
- (29) Agnoli, S.; Sambi, M.; Granozzi, G.; Schoiswohl, J.; Surnev, S.; Netzer, F. P.; Ferrero, M.; Ferrari, A. M.; Pisani, C. *J. Phys. Chem. B* **2005**, *109*, 17197-17204.
- (30) Wu, C.; Marshall, M. S. J.; Castell, M. R. *J. Phys. Chem. C* **2011**, *115*, 8643-8652.
- (31) Guimond, S.; Göbke, D.; Romanyshyn, Y.; Sturm, J. M.; Naschitzki, M.; Kühlenbeck, H.; Freund, H.-J. *J. Phys. Chem. C* **2008**, *112*, 12363-12373.
- (32) Gu, X.-K.; Ouyang, R.; Sun, D.; Su, H.-Y.; Li, W.-X. *ChemSusChem* **2012**, *5*, 871-878.
- (33) Zeuthen, H.; Kudernatsch, W.; Merte, L. R.; Ono, L. K.; Lammich, L.; Besenbacher, F.; Wendt, S. *ACS Nano* **2015**, *9*, 573-583.
- (34) Kudernatsch, W.; Peng, G.; Zeuthen, H.; Bai, Y.; Merte, L. R.; Lammich, L.; Besenbacher, F.; Mavrikakis, M.; Wendt, S. *ACS Nano* **2015**, *9*, 7804-7814.
- (35) Prada, S.; Giordano, L.; Pacchioni, G.; Noguera, C.; Goniakowski, J. *J. Chem. Phys.* **2014**, *141*, 144702.
- (36) Greeley, J.; Mavrikakis, M. *J. Am. Chem. Soc.* **2002**, *124*, 7193-7201.
- (37) Greeley, J.; Mavrikakis, M. *J. Am. Chem. Soc.* **2004**, *126*, 3910-3919.
- (38) Zhong, W.; Liang, J.; Hu, W.; Cao, X.; Jia, C.; Jiang, J. *Phys. Chem. Chem. Phys.* **2016**, *18*, 9969-9978.
- (39) Ivanov, K.; Dimitrov, D.; Boyanov, B. *Chem. Eng. J.* **2009**, *154*, 189-195.
- (40) Macquarrie, D. *Appl. Organomet. Chem.* **2005**, *19*, 696-696.
- (41) Dumesic, J. A. In *The Microkinetics of Heterogeneous Catalysis*. American Chemical Society: Washington, DC, 1993.
- (42) Chen, J.-F.; Mao, Y.; Wang, H.-F.; Hu, P. *ACS Catal.* **2016**, *6*, 7078-7087.
- (43) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
- (44) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15-50.
- (45) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169-11186.
- (46) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758-1775.
- (47) Blöchl, P. E.; Jepsen, O.; Andersen, O. K. *Phys. Rev. B* **1994**, *49*, 16223-16233.

- (48) Anisimov, V. I.; Zaanen, J.; Andersen, O. K. *Phys. Rev. B* **1991**, *44*, 943-954.
- (49) Vladimir, I. A.; Aryasetiawan, F.; Lichtenstein, A. I. *J. Phys.: Condens. Matter* **1997**, *9*, 767-808.
- (50) Spiridis, N.; Zając, M.; Piekarz, P.; Chumakov, A. I.; Freindl, K.; Goniakowski, J.; Kozioł-Rachwał, A.; Parliński, K.; Ślęzak, M.; Ślęzak, T.; Wdowik, U. D.; Wilgocka-Ślęzak, D.; Korecki, J. *Phys. Rev. Lett.* **2015**, *115*, 186102.
- (51) Alavi, A.; Hu, P.; Deutsch, T.; Silvestrelli, P. L.; Hutter, J. *Phys. Rev. Lett.* **1998**, *80*, 3650-3653.
- (52) Michaelides, A.; Hu, P. *J. Am. Chem. Soc.* **2001**, *123*, 4235-4242.
- (53) Liu, Z.-P.; Hu, P. *J. Am. Chem. Soc.* **2003**, *125*, 1958-1967.
- (54) Wang, G.-C.; Tao, S.-X.; Bu, X.-H. *J. Catal.* **2006**, *244*, 10-16.
- (55) Cheng, J.; Hu, P.; Ellis, P.; French, S.; Kelly, G.; Lok, C. M. *J. Phys. Chem. C* **2008**, *112*, 1308-1311.
- (56) Cheng, J.; Hu, P. *J. Am. Chem. Soc.* **2008**, *130*, 10868-10869.
- (57) Chorkendorff, I.; Niemantsverdriet, J. W. In *Concepts of Modern Catalysis and Kinetics*. Wiley-VCH: Weinheim, Germany, 2003.
- (58) Stegelmann, C.; Andreasen, A.; Campbell, C. T. *J. Am. Chem. Soc.* **2009**, *131*, 8077-8082.
- (59) Pulido, A.; Concepción, P.; Boronat, M.; Corma, A. *J. Catal.* **2012**, *292*, 138-147.
- (60) Xu, Y.; Mavrikakis, M. *J. Phys. Chem. B* **2003**, *107*, 9298-9307.
- (61) Parker, D. H.; Koel, B. E. *J. Vac. Sci. Technol. A* **1990**, *8*, 2585-2590.
- (62) Liu, S.; Jin, P.; Zhang, D.; Hao, C.; Yang, X. *Appl. Surf. Sci.* **2013**, *265*, 443-451.
- (63) Elias, J. S.; Artrith, N.; Bugnet, M.; Giordano, L.; Botton, G. A.; Kolpak, A. M.; Shao-Horn, Y. *ACS Catal.* **2016**, *6*, 1675-1679.
- (64) Aryanpour, M.; Khetan, A.; Pitsch, H. *ACS Catal.* **2013**, *3*, 1253-1262.
- (65) Plessow, P. N.; Bajdich, M.; Greene, J.; Vojvodic, A.; Abild-Pedersen, F. *J. Phys. Chem. C* **2016**, *120*, 10351-10360.
- (66) Fester, J.; Bajdich, M.; Walton, A. S.; Sun, Z.; Plessow, P. N.; Vojvodic, A.; Lauritsen, J.

V. *Top. Catal.* **2016**, 1-10.