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SURFACE SCIENCE

Surface Science 601 (2007) 4873-4880

www.elsevier.com/locate/susc

Oxidation of CO on Fe₂O₃ model surfaces

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Received 6 May 2007; accepted for publication 1 August 2007 Available online 31 August 2007

Abstract

Using first principles calculations based on a gradient corrected density functional formalism we show that Fe_2O_3 nano-particles with (100) and (0001) surface orientations can oxidize CO to form CO₂ with or without the presence of O₂. However, depending on the surface orientation, the oxidation occurs through differing sequences. On the (100) surface, in the absence of O₂, two CO molecules are required for one CO oxidation in a concerted reaction while on a oxygen terminated (0001) surface, a single CO molecule itself, without the aid of a second CO, can react with the lattice oxygen atoms to form CO₂. In the presence of O₂, the O vacancies created by an initial oxidation through lattice oxygen act as the favored sites for O₂ adsorption which can subsequently oxidize the incoming CO. Detailed reaction paths and the corresponding energetics for the proposed mechanisms are also studied. © 2007 Elsevier B.V. All rights reserved.

Keywords: Density functional calculations; Iron oxide; Nano-particles; Catalysis; Carbon monoxide; Oxidation

1. Introduction

The oxidation of CO is one of the most studied heterogeneous chemical reactions. The notable catalysts include transition metal surfaces, free transition metal clusters, and more recently, transition and noble metal clusters/ nano-particles supported on Al₂O₃, SiO₂, TiO₂, Fe₂O₃ and other oxide surfaces [1-10]. The oxidation generally proceeds via either of the two following mechanisms. In most cases, it proceeds via the so called Langmuir-Hinshelwood (L-H) mechanism where the reacting species are first adsorbed before undergoing the reaction. This involves formation of an intermediate complex and then desorption of the CO_2 molecule. While the L-H mechanism is the most dominant, it has recently been suggested that the oxidation of CO in some cases and in particular on Ru (0001) surface proceeds via Elay-Rideal (E-R) mechanism where O_2 is first dissociatively adsorbed on the surface. The gas phase CO molecules subsequently undergo an oxidation

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via the detachment of the adsorbed O atoms without CO being first adsorbed on the surface. Irrespective of the mechanism, the key steps in the reactions are, (1) the weakening or breaking of the O–O bond in the adsorbed O_2 molecules and (2) the formation of the CO₂ molecule. This suggests that it may be possible to avoid O–O bond breaking by considering materials that contain oxygen without O–O bonds.

An important class of materials that are rich in oxygen and yet contain O atoms with no O–O bonds is the metal oxides [11,12]. They are characterized by a charge transfer from the metal to the O atoms that are bonded only to metal sites. Since the breaking of the O–O bond in O₂ molecules is one of the key steps in oxidation of CO, it raises the question whether one can use metal oxides to accomplish the required task. Experiments [13–15] carried out over the past few years indicate that Fe₂O₃ nano-particles can indeed oxidize CO to CO₂. The oxidation of CO is found to proceed even in the absence of external O₂ and hence the nano-particles can act both as oxidizers as well as catalysts. However, the microscopic mechanism underlying this conversion is still not understood. In order to

^{0039-6028/\$ -} see front matter @ 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.susc.2007.08.015

elucidate some of these questions, two of the present authors carried out theoretical studies [16-18] on the possible oxidation of CO via a free Fe₂O₃ cluster. They showed that a free Fe₂O₃ cluster can oxidize CO in the absence or presence of O_2 . In the absence of O_2 , it is the host O atoms that take part in the oxidation of CO via the E-R mechanism. Here, the first CO is adsorbed on a Fe site of the cluster and weakens one of the Fe-O bonds. A subsequent CO molecule can bind to the weakly bound O forming a CO₂. In the presence of O_2 , the reaction proceeds via a novel process where partial CO adsorption facilitates the reaction and the system goes back and forth between the reduced and the oxidized state. What is most interesting is that CO oxidation in clusters proceeds without any barrier. This is attributed to the flexibility in geometrical rearrangement offered by the small cluster size. While these studies are interesting, the situation in nano-particles could be different. The large size could hinder any structural re-arrangements, thus introducing reaction barriers or eliminating the pathways accessible in free clusters.

The purpose of the current paper is to examine the oxidation of CO on Fe₂O₃ surfaces with different orientations by modeling these surfaces as finite clusters. There are several issues: (1) Can these model surfaces oxidize CO through the lattice oxygen, thus offering the potential of CO reduction without the introduction of oxygen. (2) Can these model surfaces act as a catalyst in the presence of oxygen? If so, what are the underlying mechanisms for the conversion of CO? (3) Since a Fe₂O₃ nano-particle can be marked by surfaces having different crystallographic orientations, it is important to study how the catalytic processes depend on various surface orientations. This understanding is crucial since the efficiency of a catalyst can be enhanced by selecting the nano-particles with desired surface morphologies. In this work, we have carried out systematic microscopic investigation of CO oxidation in the presence and absence of external oxygen on Fe₂O₃ model surfaces with two different crystallographic orientations to answer some of these questions. In particular, we find that the reaction pathways in oxidizing the CO via surface oxygen are different for different orientations.

In Section 2 we describe our theoretical method and details of the computational procedure. The results are presented and discussed in Section 3. Section 4 contains a summary of our conclusions.

2. Theoretical method and computational procedure

Our calculations are based on density functional theory (DFT) with generalized gradient approximation for exchange and correlation potential. The interactions of CO and O2 with Fe2O3 model surfaces were studied by considering two different crystallographic orientations, namely (100) and oxygen terminated (0001) surfaces as shown in Fig. 1. It is important to note that (100) surface contains both Fe and O atoms, whereas (0001) surface, depending on the termination, can be terminated either by Fe atoms or by O atoms. In this study, we have chosen oxygen terminated (0001) surface. Finite clusters constructed by cleaving the bulk Fe_2O_3 in (100) and (0001) directions are used to model the surfaces. This choice for the geometry of the surfaces is justified by noting that even small clusters of metal oxides are known to retain the bond lengths, bond angles, and coordination of their bulk counterpart [19,20]. The dangling bonds of the edge atoms in the cluster are passivated by adding hydrogen atoms. This is customary in modeling covalently bonded materials so that the interaction of the surface atoms with the reagent molecules is not influenced by the edge atoms.

The theoretical studies were carried out using the DMol3 code [21] and the gradient corrected Becke exchange functional [22] and Perdew–Wang correlation functional [23]. Double numerical basis sets (DNP) supplemented with 4p polarization functions for Fe and 3d polarization functions for O and C were used for the atoms. The accuracy of these basis sets has been confirmed



Fig. 1. The atomic structure of (100) and oxygen terminated (0001) surfaces. Oxygen atoms are given in small spheres (dark) and iron atoms are larger spheres (grey).

in our previous studies [16,17] on CO oxidation in small Fe_2O_3 gas phase clusters. The geometry convergence criterion was set to 10^{-3} hartree/bohr and 10^{-5} hartree for gradient and energy, respectively. Our past experience has shown that these criteria are sufficient to ensure converged results.

In the following, we first present and discuss the results of our study on the interaction of CO and O_2 with the Fe₂O₃ (100) model surface. The results on CO and O_2 interaction with oxygen terminated (0001) surface orientation are reported in the latter part of the paper.

3. Results and discussion

3.1. Fe_2O_3 (100) surface orientation

The cluster considered here to mimic the Fe_2O_3 (100) surface is a $Fe_{15}O_{18}$ cluster, with nine iron and eight oxygen atoms on the top layer. All the dangling bonds of edge iron atoms were capped with hydrogen atoms so that the interaction of the reagent gas molecules with the surface atoms will not be affected due to the finite cluster used to model the surfaces. The cluster model along with the surface atoms that were allowed to relax during the geometry optimization are shown in Fig. 2.

As a first step, the relaxation of the free Fe_2O_3 (100) surface was studied by relaxing the top layer of the cluster. Only three iron atoms (labeled as Fe7, Fe8, and Fe9) and two oxygen atoms (O12 and O14) that are in the center of the top layer (see Fig. 2) were allowed to relax, while the remaining atoms are kept fixed at their initial positions. Upon relaxation, the three iron atoms (Fe7, Fe8, and Fe9) and O14 atom moved downward, while the oxygen atom (O12) bonded to the two iron atoms (Fe8 and Fe9) moved upward from their corresponding un-relaxed starting positions. The relaxation resulted in a contraction of the Fe–Fe bond length by 5% (from 2.88 to 2.74 Å), while one of the Fe–O bond lengths decreased by 14% (from 2.08 to 1.79 Å) and the other by 6.1% (from 2.08 to 1.96 Å).



Fig. 2. Finite Cluster used to model Fe_2O_3 nano-particle with (100) surface orientation. The iron and oxygen atoms that are allowed to relax during the surface relaxation are identified.

The oxidation of CO molecule via Fe₂O₃ model surface with (100) orientation was studied by adsorbing the CO molecule onto the relaxed (100) surface. Two surface atoms, namely Fe8 and O12 (see Fig. 2) of the Fe15O18 cluster, were considered as possible binding sites for the approaching CO molecule. Five surface atoms (Fe7, Fe8, Fe9, O12, and O14 in Fig. 2) of Fe₂O₃, along with the CO molecules were allowed to relax during the geometry optimization. As expected, our calculations show that the approaching CO molecule prefers to bind to the surface Fe atom (Fe8 in Fig. 2), with an optimized Fe-C distance of 1.84 Å. The C-O bond length in the CO molecule remained essentially constant at 1.15 Å. The binding of CO molecule to surface Fe atom (Fe8) resulted in the weakening of the bond between Fe8 and the surface oxygen atom (O12), where the Fe-O bond length was elongated by 3.12% to 1.85 Å. It is interesting to compare the present calculated binding energy, namely 1.25 eV, of the CO molecule to the (100) model surface with that obtained from the previous study (3.17 eV) of the interaction of CO with a free Fe₂O₃ cluster [17]. This energy difference is a reflection of the energy gain arising from the structural rearrangement of the free cluster.

A second CO molecule was now adsorbed on the (100) surface to examine if the loosely bound surface oxygen atom can oxidize this approaching CO molecule and how this in turn will affect the topology of the Fe₂O₃ (100) model surface. The approaching second CO molecule again has different sites available for adsorption on the surface: it can bind either to the iron atom (Fe9) or to the oxygen atom (O12) (whose bond with Fe8 has been weakened) on the Fe₂O₃ surface (see Fig. 3). The calculations revealed



Fig. 3. The two different binding sites (Fe9 and O12) available for the second CO molecule (top view of (100) surface).

that the binding of CO molecule to the iron atom (Fe9) is energetically not a favorable configuration. When the CO is adsorbed on the oxygen atom (O12), it formed a strong bond with the oxygen. This resulted in the formation of a CO_2 and the subsequent detachment from the surface, leaving behind an oxygen-depleted Fe2O3 surface. When the CO2 is formed, the O-C-O distance from the nearest surface Fe atom is 2.37 Å. Note that the Fe–O bond length in iron oxide molecule is calculated to be 1.61 Å. This clearly indicates that the resultant CO₂ molecule has completely detached from the Fe₂O₃ surface. Though explicit reaction barrier calculations were not performed, the process of breaking two surface Fe-O bonds and complete detachment of CO₂ molecule from the surface indicate that oxidation via surface oxygen atoms seem to have proceeded with a low energy barrier. The initial adsorption of CO and the subsequent resultant geometry during the oxidation process is shown in Fig. 4.

The oxidation of CO by the surface oxygen atom (O12), created an oxygen vacancy on the surface, which in turn resulted in a further reconstruction of the Fe₂O₃ model surface. As the iron–oxygen bonds (Fe8–O12, Fe9–O12) are broken in the oxidation process, one of the iron (Fe8) atoms moved downward towards the sub-surface layer and formed stronger bonds with the oxygen atoms. Consequently, a new bond with an iron atom in the sub-surface layer is formed. In addition, the bond length between the first CO molecule and the iron atom (Fe8) was decreased by 3.8% (from 1.84 Å to 1.77 Å), thus strengthening the Fe–CO bond slightly. However, the C–O bond of the CO molecule showed a negligible elongation of 0.01 Å (from 1.15 Å to 1.16 Å).

The above process for CO oxidation via surface oxygen atom is similar to the previously reported study [16,17] on the oxidation of carbon monoxide by a free Fe₂O₃ cluster, where the host Fe₂O₃ provided the oxygen in the formation of CO₂. The formation of CO₂ here has resulted in lowering of energy by 1.95 eV, while in the previously reported free cluster calculation [16,17] the oxidation of CO resulted in lowering of the total energy by about 1.90 eV. Thus, oxidation of the approaching CO molecule, even in the absence of oxygen, has clearly demonstrated that Fe_2O_3 (100) surface can act as an oxidizing agent.

In order to study further the role of $Fe_2O_3(100)$ surface as a catalyst in oxidizing the CO molecule, an O₂ molecule was introduced on to the now oxygen-depleted Fe₂O₃ (100) surface. The incoming O₂ molecule encounters various binding sites on the surface: (1) O_2 can bind to the first CO molecule and can form either a CO₃ complex or it can oxidize the CO leaving behind atomic oxygen on the surface; (2) it can bind to the free iron atom (Fe9) or (3) the O₂ can directly adsorb on to the oxygen-vacancy site created by the oxidation process in the previous step. In addition, the O_2 can approach the surface either with its bond axis parallel or perpendicular to the surface. All these possibilities were taken into consideration during our study. The process of the approaching O_2 forming a bond with the CO molecule on the surface resulting in either the CO₃ complex or oxidizing the CO was not observed here. In fact, when the O_2 molecule was brought closer to the CO, the O_2 moved away and formed a bond with the Fe atom. This result is in contrast to the previously reported study [16,17] on the free Fe₂O₃ cluster in which the formation of CO₃ was an energetically favorable configuration. The adsorption of O_2 with its axis perpendicular to the surface is also found to be energetically ($\Delta E = 0.45 \text{ eV}$) an unfavorable orientation. Among the above mentioned scenarios, the approaching O_2 , with its bond axis parallel to the surface, prefers to either bind to the free iron atom or adsorb near the oxygen vacancy site. The two lowest energy configurations for O₂ adsorption on the oxygen-depleted Fe₂O₃ surface, along with the relative energies are given in Fig. 5.

In the ground state configuration (Fig. 5a), the O_2 molecule was found to bind strongly with two surface iron atoms, resulting in elongation of O–O bond length to 1.41 Å, and thus weakening the O_2 bond strength.

In the other configuration, the O_2 was brought near the free Fe atom, with its bond axis parallel to the surface. Upon relaxation, it was found that the bond axis of O_2 is no longer parallel to the surface and one of the oxygen atoms formed a bond with the surface Fe. The second



Fig. 4. The formation and subsequent detachment of CO_2 molecule from the Fe_2O_3 . Carbon, oxygen (small spheres) and iron (larger spheres) atoms are shown in grey, red and violet, respectively. Edge hydrogen atoms are not shown for clarity purposes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A.K. Kandalam et al. | Surface Science 601 (2007) 4873-4880



Fig. 5. Top view of the two lowest energy configurations corresponding to O_2 adsorption on oxygen-depleted Fe_2O_3 surface. Oxygen atoms (small spheres) are shown in red color, whereas iron atoms (larger sphere) are shown in violet. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

oxygen atom, while occupying a site very close to the oxygen-vacancy site remained weakly bound to the Fe atom in the second layer (see Fig. 5b). The adsorption of O_2 resulted in the weakening of the O–O bond strength, with a bond elongation of about 4.6%. This weak O–O bond facilitates the oxidation of the subsequent approaching CO molecule. The binding energy of the O_2 molecule with the oxygen-depleted (100) surface is 4.04 eV. The depletion of oxygen from the (100) surface in the earlier reaction step leaves the neighboring Fe atom in a higher positive valence state. Hence, the approaching O_2 molecule binds very strongly to the Fe atom, which is reflected in the large binding energy of O_2 with the surface Fe atoms.

The introduction of a third CO molecule is seen as the next logical step towards understanding the role of Fe_2O_3 (100) as a catalyst in the oxidation of CO in the presence of O_2 . The second configuration (Fig. 5b), in which one of the oxygen atoms is loosely bound to the sub-surface Fe atom, is best suited for this investigation. When a third CO is introduced near the oxygen molecule deposited on the (100) surface, it gets oxidized immediately by binding with the oxygen atom which has a very weak bond with one of the sub-surface iron atom. Consequently, the original composition of the (100) surface with the first CO attached to the surface iron atom is restored (see Fig. 6). The relative energies of various stages of the reaction processes discussed above are collected in Table 1 for clarity.

Thus, this study has clearly demonstrated that Fe_2O_3 (100) surface has the potential to act as a catalyst in the presence of oxygen, and as an oxidizing agent in the absence of oxygen, thereby facilitating the oxidation of carbon monoxide both in the presence as well as absence of oxygen.

3.2. Fe_2O_3 (0001) surface orientation

In this section, we present the results of the oxidation of the CO molecule on the oxygen terminated Fe_2O_3 (0001) surface. The finite cluster employed to mimic the oxygen terminated (0001) surface consists of four layers with oxygen and iron atom layers arranged in alternative fashion. It consists of a total of 43 atoms ($Fe_{20}O_{23}$ cluster). The top and side views of the (0001) surface model are shown in Fig. 7.

To study the relaxation of the $Fe_{20}O_{23}$ (0001) model surface we allowed six surface oxygen atoms and four sub-surface iron atoms in the cluster to relax (see Fig. 7). Four of the surface oxygen atoms in the center moved inward by 0.32 Å while the other two moved inward by 0.22 Å from their bulk positions. The strong inward movement of surface oxygen atoms observed here is in good agreement with a previously reported VASP based slab calculation [24] on fully oxidized (0001) surface. The relaxation of the iron atoms in the sub-surface layer led to the elongation of bond between sub-surface iron and 3rd layer oxygen atoms.

We now present our results on the interaction of CO molecule with the relaxed (0001) surface. Note that the CO molecule has two surface sites available on the (0001) surface, namely, the on-top site above the oxygen atom and a bridge site between two surface oxygen atoms. The optimized geometries of both the configurations are shown in Fig. 8. In the first configuration (henceforth referred to as configuration – I), when the CO molecule approached the bridge site on the surface, the carbon monoxide molecule bonded with both of the surface oxygen atoms; and thereby formed a CO_3 complex (see

A.K. Kandalam et al. | Surface Science 601 (2007) 4873-4880



Fig. 6. Catalytic oxidation of CO molecule on the (100) surface. Edge hydrogen atoms are not shown for clarity purposes.

 Table 1

 Relative energies of various stages of reaction processes on (100) surface

Reaction	Energy gain (eV
$Fe_2O_3 + CO \rightarrow (Fe_2O_3)CO$	1.25
$(Fe_2O_3)CO + CO \rightarrow (Fe_2O_2)CO + CO_2 (g)$	1.95
$(Fe_2O_2)CO + O_2 \rightarrow [(Fe_2O_2)CO]O_2$	4.04
$[(Fe_2O_2)CO]O_2 + CO \rightarrow (Fe_2O_3)CO + CO_2 (g)$	0.38

 (Fe_2O_3) represents the (100) surface, (Fe_2O_2) represents oxygen atom depleted (100) surface; while CO_2 (g) corresponds to CO_2 molecule leaving the surface after formation.

Fig. 8). The binding energy of the CO molecule to the (0001) surface is calculated to be 2.26 eV. It is quite clear from the optimized geometry of configuration – I, that formation of CO₂ and subsequent detachment from the surface has a definite reaction barrier.

In the second configuration (configuration – II), the CO molecule was allowed to adsorb directly onto one of the surface oxygen atoms. In this case, it was observed that the CO formed a strong bond with the surface oxygen leading to the formation of CO_2 (see Fig. 8). The formation of

the new oxygen–carbon bond weakened the surface oxygen-subsurface iron bond substantially, but did not break it. Again, unlike in the case of (100) surface oxidation, the newly formed CO_2 did not detach from the surface completely. This configuration is 0.52 eV higher in energy than the first configuration. Though, the formation of CO_3 complex is thermodynamically preferred, depending on the experimental conditions, and the high temperatures involved in these reactions, one cannot conclusively rule out the possibility of attaining configuration – II in the experiments, and hence a direct CO oxidation.

The stability and the possibility of CO_2 formation in these systems have been studied further by calculating different dissociation pathways. The stability of a given configuration against dissociation into CO_2 and oxygendepleted surface is calculated by the following equation:

$$-[E(Fe_2O_3-CO) - E(oxygen-depleted Fe_2O_3) - E(CO_2)]$$

It is found that the formation of CO_2 in configuration – I is an endothermic reaction, and requires 0.36 eV of energy.



Fig. 7. The top view and side view of the oxygen terminated (0001) surface. Red (smaller) spheres denote oxygen atoms and violet (larger) spheres denote iron atoms. The atoms that are allowed to relax are identified by arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A.K. Kandalam et al. | Surface Science 601 (2007) 4873-4880



Fig. 8. The optimized geometries of two different configurations obtained from two different surface site adsorption of CO.

On the other hand, configuration – II is thermodynamically unstable against the dissociation of CO_2 from its surface by 0.15 eV.

It is important to note here that the adsorption of CO molecule in configuration – I is highly exothermic (2.26 eV), while the dissociation of configuration – I and formation of CO₂ is slightly endothermic (0.36 eV). Hence, in a real experimental situation, it is expected that the energy liberated from the adsorption process can overcome the small endothermicity and the energy barrier and finally result in the liberation of CO₂, giving rise to an energy gain

of 1.90 eV. However, in order to come to a definite conclusion on this reaction, one has to investigate the temperature effects using molecular dynamics, which is beyond the scope of this paper. In summary, two different possible mechanisms are operating in the oxidation of CO via surface oxygen on the (0001) surface. The first one proceeds through a stable reaction intermediate, namely CO₃, which in turn, at high temperatures, can dissociate to liberate CO₂ (configuration – I). The other one is a direct attack of CO on the surface oxygen atom resulting in the formation of CO₂ (configuration – II). The oxidation of CO via surface



Fig. 9. The starting and optimized geometries of O_2 adsorption onto oxygen-depleted (0001) surface. The relative energies of the two configurations are also shown.

oxygen in configuration – I is similar to Langmuir–Hinshelwood (L–H) mechanism, where an intermediate complex is formed before desorption of CO_2 .

In order to study the catalytic behavior of the (0001) surface, we have introduced an O₂ molecule onto the oxygen-depleted surface. It was found that the O₂ prefers to adsorb onto the surface with its bond axis perpendicular to the surface. The configuration where oxygen is adsorbed with its bond axis parallel to the surface is 0.22 eV higher in energy (see Fig. 9). The low coordinated oxygen atom in the perpendicularly adsorbed O₂ molecule (Fig. 9a) becomes the active site. When a CO molecule approaches this active site, it gets oxidized and completely desorbs from the surface. The resulting catalytic reaction is calculated to be exothermic in nature with an energy release of 3.81 eV.

4. Summary and conclusions

The present studies show that Fe₂O₃ nano-particles with (100) orientation can oxidize a CO molecule via surface oxygen atoms. While the desorption of CO₂ from the (100) surface can be spontaneous, that on the (0001) surface will encounter an energy barrier. Overall, three different processes are observed in regards to CO₂ formation via surface oxygen: On (100) surface, a second CO molecule can be oxidized by directly picking up one of the surface oxygen atoms (E-R mechanism), whereas the CO oxidation on the (0001) orientation would proceed via two different mechanisms; one a direct oxidation and the other a two step procedure (L-H mechanism). The energy gain due to CO_2 formation, via surface oxygen, in both the (100) and (0001) surfaces are close to each other (1.96 eV and 1.90 eV, respectively). Therefore, from purely energetics view point and at high temperatures, both the surfaces have the potential to act as oxidizing agents. The different reaction pathways observed in (100) and (0001)surfaces are due to different surface energies and surface atomic structure.

The above conclusions are based on cluster models of the surfaces and one may wonder if the conclusions depend on the cluster size. As we have indicated earlier, in metal oxides, due to strong covalent bonding, very small clusters bear the signature of their bulk [19,20]. In addition, conclusions reached here are consistent with those in free clusters where all atoms were allowed to relax. Thus, one could argue that the size of the cluster we have used to model the surface is adequate to provide a qualitative understanding of the role surface orientations play in the CO oxidation.

Acknowledgment

The authors are thankful to Philip Morris USA for partial support.

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