Applied Physics Letters

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Cite as: Appl. Phys. Lett. **97**, 233108 (2010); https://doi.org/10.1063/1.3525372
Submitted: 02 November 2010 . Accepted: 17 November 2010 . Published Online: 09 December 2010

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APPLIED PHYSICS LETTERS **97**, 233108 (2010)

Rational computational design of optimal catalytic surfaces

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(Received 2 November 2010; accepted 17 November 2010; published online 9 December 2010)

Using calculations from first-principles based on density functional theory, we introduce an innovative concept for the design of catalysts based on the tuning of the surface properties by progressive layering of thin metal films on an oxide support, where the substrate is substantially exploited as an active design element for the tuning of the reactivity of the metallic surface. We demonstrate this idea by studying the adsorption and activation properties of CO_2 on Pd and oxide-supported Pd thin films. © *2010 American Institute of Physics*. [doi:10.1063/1.3525372]

Over the past century, we have accumulated a vast empirical knowledge of catalysis and catalysts for an enormous number of reactions. However, it is only recently that we are moving away from this empirical approach and we are attempting a rational design of materials tailored to specific reactions. In this paper, we address the problem of the first-principles design of catalytic surfaces for the activation and reduction of carbon dioxide. In general terms, we are looking at a reaction that has two main parts: the dissociation of the reacting CO_2 molecule and the removal, and/or further activation of the dissociation products. Following Sabatier,[1] small activation energy and a weak bonding of the intermediates should characterize an optimal catalyst for this reaction. It has been demonstrated, at least in the case of the dissociation of diatomic molecules, that there is a universal, reactant independent relation between the reaction activation energy and the stability of reaction intermediates. This directly leads to a universal relationship between adsorption energies and catalytic activity, which is used to pinpoint what it is that determines the best catalyst for a given reaction.[2] This universality has to be necessarily linked to the electronic properties of the reacting surface, so understanding the interplay between structure and properties opens the way toward the rational design of catalytic systems.

In previous investigations, we have been able to illustrate how one of the central issues in the control of electronic properties of materials is the role of interfaces.[3] In particular, understanding the formation of and the ability to tune the Schottky barrier in metal-oxide insulator interfaces (the energetic barrier the electrons have to overcome to go from the valence band of the metal to the conduction band of the oxide) is of paramount importance for the design of metallic surfaces that can be engineered to have specific catalytic properties.[3] Indeed, a thin metallic layer on an oxide surface substantially differs from the ideal crystalline termination of the bulk metal. Its geometry is dictated by the surface atomic configuration, and the bonding with the substrate drastically affects the electronic properties of the film. The very existence of this layer opens up the possibility of using it for the manipulation of the electronic properties of the heterojunction. Indeed, this interface phase can act as a "Coulomb buffer" that constrains the physical structure of the junction and sets the electrical and magnetic boundary conditions that establish the junction electronic and thus catalytic properties.[4] The core of our innovative concept for the design of catalysts is the conceptual system depicted in Fig. 1, where we introduce the prototypical case of carbon dioxide adsorption and dissociation on specifically tailored Pd thin films supported on an oxide substrate. In general, for oxide-supported metal particles catalysts, the support serves as a structural promoter that, in combination with the metal deposition conditions, determines the size and shape of the catalyst particles and thereby exposes the types of the metal atom faces.[5] In our design, we have introduced the additional degrees of freedom that come from the interface between the thin metal layer and the surface used as support.

The interaction of CO_2 with transition metal surfaces has been extensively studied, since metallic nanostructures are routinely used in the heterogeneous catalysis of carbon dioxide.[6] CO_2 has several possible modes of coordination with a metallic surface: pure carbon coordination, pure oxygen coordination or mixed carbon-oxygen coordination, and the molecule can either be chemisorbed or physisorbed. The chemisorbed state is related to the formation of ${CO_2}^{\delta-}$, where an electronic charge transfer occurs from the metal to the molecule. In what follows, we will demonstrate how one can dramatically improve upon the catalysis of CO_2 via the control of the metallic surface at the nanoscale.

The results presented in this work were obtained using plane-wave, pseudopotential, density functional theory as implemented in the QUANTUM-ESPRESSO software package.[7] We used both the local density approximation (LDA) with the Perdew–Zunger exchange-correlation functional[8] and generalized gradient approximation (GGA) with the Perdew–Becke–Ernzerhof functional[9] in order to test the reliability of our conclusions. Higher order exchange-correlation functionals (BLYP, meta-GGAs, B3LYP, etc.) will produce results that are intermediate between the LDA and GGA reported here. We used ultrasoft pseudopotentials[10] and an 881 k-point mesh for the Brillouin zone integration in a supercell geometry. All structures have been relaxed to forces less than 0.01 eV/Å. In order to prevent interaction between periodic images in the z-directions we used a vacuum of 14 Å in a symmetric supercell.[11] Calculations are done at 1/8 ML coverage of CO_2, i.e., one molecule per eight surface atoms to minimize spurious lateral interactions. Reaction pathways

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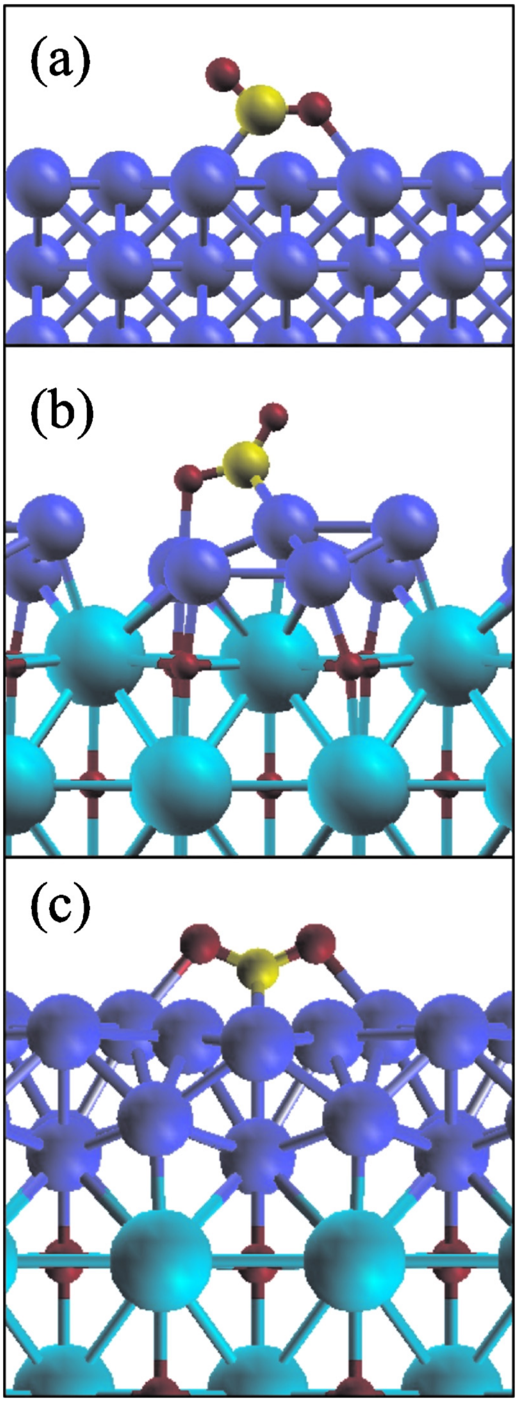

FIG. 1. (Color online) Geometry of the catalytic surface and most stable chemisorption geometries of CO_2 for three different configurations: (a) bulk metal, (b) metal monolayer on oxide, and (c) metal bilayer on oxide. Blue atoms are Pd (top layers), cyan is Ba, and red is O (bottom layers).

and activation barriers were obtained using the nudged elastic band method with the climbing image modification.[12]

We have demonstrated our concept of interfacial tuning of the catalytic activity by studying the prototypical case of activation and dissociation of CO_2 on Pd. In particular, we have calculated the chemisorption, dissociation, and activation energy (the simplest descriptors of catalytic activity) on the clean (001) face of Pd, and compared it with the properties of a thin film of variable thickness of the same metal on a substrate of BaO, which is a simple binary oxide (see Fig. 1), in order to address the role of the substrate localized

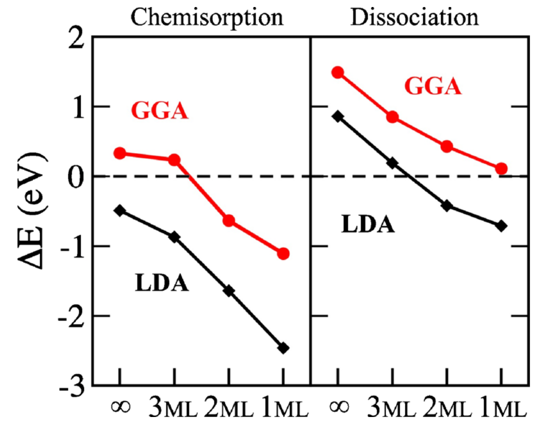

FIG. 2. (Color online) Chemisorption and dissociation energies ($CO_2 \rightarrow CO+O$) for CO_2 on Pd for two choices of density functionals and different geometries: bulk metal (∞), 1 through 3 monolayers on the oxide substrate (xML).

charge and of the atomic and molecular electronic states on the adsorption and dissociation cross section for CO_2.

The adsorption (and dissociation) energy for the molecule can be easily computed from the knowledge of the energy of the individual components of the reaction

$$\Delta E_{A(D)} = E(CO_2 + \text{surface}) - E(\text{surface}) - E(CO_2),$$

where $E(CO_2+\text{surface})$ is the energy of the product, and E(surface) and $E(CO_2)$ are the energies of the reactants: an isolated linear CO_2 molecule and the clean surface. Once chemisorbed, the molecule can dissociate into CO+O, with both products bonded to the surface atoms, and the dissociation energy is computed along the same lines as above, with CO+O+surface as the product. The results of these relatively simple calculations demonstrate already the effectiveness of the design approach we have envisioned: indeed, by modifying the structure of the catalyst by introducing the oxide interface as functional parameter we achieve an amazing tunability of the adsorption energetics. In Fig. 1, we display the different geometries of the interfacial systems, while in Fig. 2, we report the energetics of chemisorption and dissociation calculated using different approximation for the exchange-correlation functional in DFT. The fact that two different functionals (local density approximation or LDA, which is known to overestimate the bonding strength, and the generalized gradient approximation, GGA, which is known to underestimate it) give the same qualitative behavior strongly confirms the reliability and robustness of our findings and interpretations. The adsorption of CO_2 increasingly becomes more exothermic when the molecule interacts with a thinner metallic film on the oxide support. In the limit of 1 ML, CO_2 makes strong bonds with the surface atoms and the metallic monolayer is highly perturbed by the adsorption of the molecule. Clearly, the underlining polar distribution of charge at the metal-oxide interface is responsible for the drastic change in the interaction characteristics. However, this interaction strength can be readily controlled by the selective growth of thicker films, as shown by the 2 and 3 ML cases, where the adsorption of the CO_2 molecule is still exothermic, but with a progressively lower binding energy.

Indeed, these results demonstrate that by modifying the structure of the catalyst with the introduction of the oxide interface as a functional parameter, we achieve an amazing

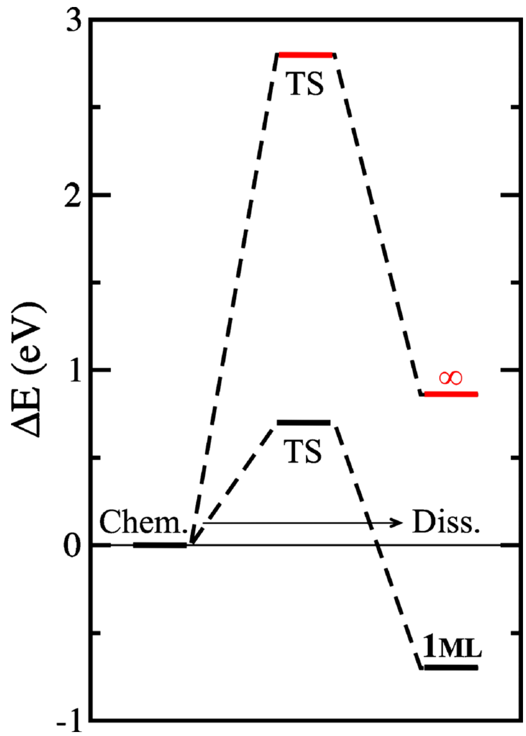

FIG. 3. (Color online) Energy diagram for adsorption, dissociation and relative barriers of CO_2 on the (001) surface of a bulk Pd metal (red/lighter gray) and on a monolayer Pd film of BaO (black). TS indicates the transition state energy as computed via the nudged elastic band algorithm. As a reference, the dissociation energy for CO_2 in free space is 8.75 eV. Data reported in the figure are for the LDA exchange and correlation functional. Similar qualitative results are obtained using GGA. Their qualitative agreement strongly corroborates the conclusions of our investigation.

tunability of the reaction energetics. The results unequivocally prove that both chemisorption and dissociation are increasingly favorable as the interface layer is made closer to the reactive surface, a clear indication of the influence of the underlining polar distribution of charge at the metal-oxide interface. Here, the role of the oxide support is not merely morphological but also functional since the distribution of the charge on the oxide surface. Its microscopic dipoles create the charge dishomogeneity and patterning that favor an enhanced catalytic activity.

Moreover, this interaction strength can be readily controlled by the selective growth of thicker films. The same effect is observed in the activation barrier for dissociation, where we compute a decrease of more than a factor of 3 in the barrier height going from the bulk metal to 1 ML of Pd on BaO as reported in Fig. 3. The enhancement of reactivity of the metal atoms on the oxide interface is clearly related to the realignment of the electronic states induced by the interfacial dipoles, and it is clearly of a universal nature. Metallic nanoparticles on polar substrates see an enhancement in catalytic activity that can be clearly interpreted in the framework of the Coulomb buffer effect.[13]

From here, one can easily envision the exploitation of the added functionalities of complex multifunctional materials such as ferroelectricity[14] and magnetism[15] to bring the tuning of the catalytic surface to the highest level of control. By combining all these aspects, one can reach the ultimate goal of designing multifunctional catalysts that, depending on the external conditions, would be able to catalyze more than one chemical reaction, a fundamental requirement for the development of advanced catalytic processes and a concept that has broad implications for the design of "green" and sustainable chemistry cycles.

This work has been supported in part by NSF and by BES, U.S. DOE at ORNL (Contract Nos. DE-FG02-98ER14847 and DE-AC05-00OR22725 with UT-Battelle, LLC). Calculations have been carried out at NCCS-ORNL.

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