Pre-Adsorbed Promoters on Dilute Palladium-Gold Alloys for the Oxidative and Non-Oxidative Upgrade of Methane

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Introduction

The grandest challenge in the direct conversion of methane to useful products is finding a catalyst that is active for the difficult C-H bond scission step [1], yet selective such that not all of the C-H bonds break to generate coke or CO_2. These requirements inevitably lead to the downfall of single transition metals, such as palladium and gold. Palladium is highly active for the C-H bond scission of methane, but the dehydrogenation is carried out to completion [2], indicating poor selectivity. Meanwhile, gold is selective for methane activation because the methyl adsorbate would rather desorb than dehydrogenate further [3], but breaking the initial C-H bond of the inert methane is the greatest obstacle, which illustrates the metal's poor activity.

After decades of research, more innovative and unconventional strategies are needed for the selective activation of methane. In this work, we combine two approaches that break convention and provide different routes for the initial C-H bond scission. The first approach involves the utilization of isolated atomic surface configurations, which limits ensemble effects. By alloying of dilute amounts of palladium into a gold host, a surface configuration where a highly active promoter atom is fully surrounded by less active host atoms can be created. The second approach consists of leveraging pre-adsorbed oxygenate promoters to alter the reaction pathways for methane activation. Using density functional theory (DFT), these two approaches are merged and used synergistically to improve both the non-oxidative and oxidative activation pathways of methane.

Materials and Methods

All periodic DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) The core and valence electrons were represented using the projector augmented wave (PAW) method with an energy cutoff of 400 eV. The exchange and correlation were described by the Perdew-Wang (PW91) functional. All geometries were optimized until the residual forces on each atom were converged below 0.02 eV/Å. Three different surfaces were examined: Pd(111), Au(111), and $Au_3Pd(111)$. The stable $Au_3Pd(111)$ alloy was chosen because Pd remained dilute enough within the alloy such that it was fully surrounded by Au atoms on the surface. For the oxidative methane activation schemes, O*, O_2*, OH*, and OOH* were pre-adsorbed onto the three surfaces, and the climbing-image nudged elastic band (CI-NEB) method was used to determine the locations and energies of transition states.

Results and Discussion

In the non-oxidative activation of methane, we find that $Au_3Pd(111)$ exhibits activity similar to that of Pd(111), with a slightly higher activation energy barrier for the initial C-H bond activation. After the first dehydrogenation step of methane to methyl, however, $Au_3Pd(111)$ more resembles Au(111), where the subsequent dehydrogenation steps are more difficult than the first, as depicted in the potential energy diagram in Figure 1(a). Thus, in the non-oxidative activation of methane, the first approach of isolated atom surface geometries in $Au_3Pd(111)$ is successful because it maintains high activity from the single Pd atom, yet avoids coking, which is a symptom of large Pd ensembles.

In the oxidative activation of methane, we find that facilitating the formation of certain oxygen-containing promoters greatly improves activity on Au(111). Due to the inherent weak interactions, however, it is difficult to bind the pre-adsorbates onto Au. Our DFT simlations suggest that the dilute Pd surface atoms act as collectors for the oxygenate adsorbates; O_2 binds to the Pd atom, splits into 2 O*, and assists in the activation of methane. Since the Pd atom is blocked by the newly-formed OH*, the resulting methyl resides on an Au top site, where it is selective for further chemistry. The activity of the oxidative activation of methane on $Au_3Pd(111)$ is compared to its constituent single metals in the potential energy diagram in Figure 1b, which shows that the alloy avoids coking or CO_2 formation seen on Pd(111) while allowing an exothermic binding step for the O_2 adsorption to promote the C-H bond scission. Therefore, in the oxidative activation of methane on $Au_3Pd(111)$, both the ensemble effect and the tuning of surface coverages work synergistically to provide reaction pathways that exhibit the selectivity of Au(111) while greatly improving upon its activity.

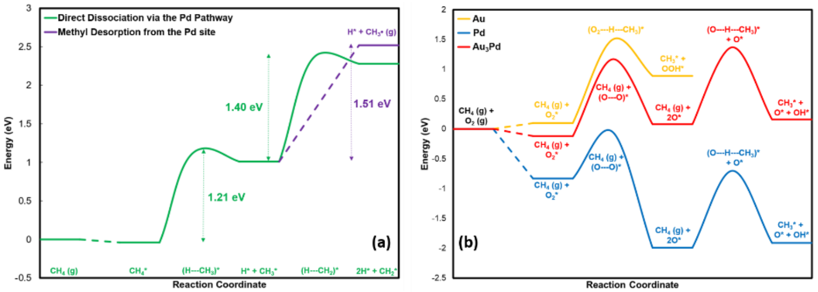

Figure 1. The potential energy diagrams for the (a) non-oxidative dehydrogenation of methane on $Au_3Pd(111)$ and (b) oxidative activation of methane on all three surfaces.

Significance

This work explores two innovative strategies to alter the reaction pathways and improve the activity and selectivity for the initial C-H bond scission in methane activation, which is a highly desirable elementary step. These strategies can be further expanded to include similarly difficult C-H bond activations for other hydrocarbons as well; this may be of interest for industrial dehydrogenation reactions, such as the dehydrogenation of propane to propylene.

References

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