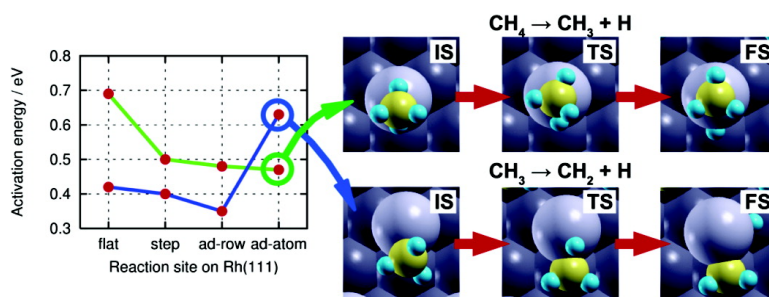


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## Engineering the Reactivity of Metal Catalysts: A Model Study of Methane Dehydrogenation on Rh(111)

Anton Kokalj,<sup>\*,†,#</sup> Nicola Bonini,<sup>†</sup> Carlo Sbraccia,<sup>†</sup> Stefano de Gironcoli,<sup>†</sup> and Stefano Baroni<sup>†</sup>

Scuola Internazionale Superiore di Studi Avanzati (SISSA) and INFN DEMOCRITOS National Simulation Center, Via Beirut 2-4, 34014 Trieste, Italy, and Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Received August 10, 2004; E-mail: tone.kokalj@ijs.si

Tuning the relative reaction rates of the different steps of methane dehydrogenation would allow for the optimization of the design of important chemical processes such as, for example, the production of hydrogen from methane or the conversion of the latter to methanol. The efficiency of transition-metal catalysts to promote these and other related reactions is limited by the tendency of dehydrogenation to proceed until graphite is eventually formed on the surface, thus poisoning the catalyst.

The importance of surface defects in determining the reactivity of heterogeneous catalysts can hardly be overestimated.<sup>1</sup> Not only do defects usually bind adsorbates more strongly than perfect facets do, but in certain cases they may dominate the reactivity of the catalyst even at very low concentrations.<sup>2</sup> The ability to control the type and concentration of surface defects would thus provide new and extremely powerful ways to tailor the chemical reactivity of transition-metal catalysts.

Motivated by these considerations, we have investigated the first two steps of methane dehydrogenation on Rh(111) using density-functional theory,<sup>3</sup> focusing on the dependence of the catalyst's reactivity on the atomic coordination of the active metal site. Our main result is that, although the barrier for the dehydrogenation of methane ( $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ ) decreases as expected with the coordination ( $N_C$ ) of the binding site, the dehydrogenation of methyl ( $\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$ ) is hindered at an ad-atom site, where the first reaction is instead the most favored.

Four different reaction sites were considered (see Figure 1): an atom at a (111) clean facet ( $N_C = 9$ ); at the edge of a (100) step therein ( $N_C = 7$ ); at an added row ( $N_C = 5$ ), and an ad-atom ( $N_C = 3$ ). For each one of these sites, we have first determined the optimal adsorption geometries and energies of the reactants and products.<sup>4</sup> In Figure 2, we report the adsorption energies calculated for the various chemical species involved in the reactions. Note that the adsorption of  $\text{CH}_4$ ,  $\text{CH}_3$ , and  $\text{CH}_2$  is rather sensitive to the coordination of the metal binding site, whereas the adsorption of hydrogen is not much so. The adsorption energy of methane is very small, smaller in fact than the accuracy expected from current density functionals that do not account for dispersion forces. Notwithstanding, the differences among the adsorption energies of different chemical species, as well as of a same species for different adsorption sites, are well within the current predictive power of density functional theory.

The identification of the minimum-energy path<sup>5</sup> connecting the initial (IS) and final (FS) states allows for the characterization of the reaction mechanism, as well as for the location of the transition state (TS) and for the determination of the activation barrier,  $E^*$ . As an example, in Figure 3 we report the IS, TS, and FS structures for the two reactions occurring at an ad-atom defect. In the case of methane dissociation on a (111) facet, methane in the IS is quite

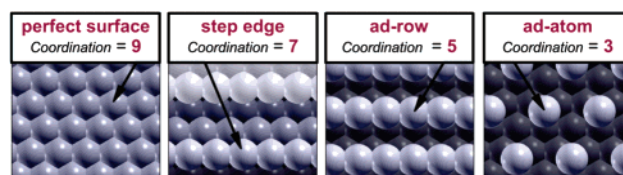


Figure 1. Different local geometries of the reaction site on Rh(111). From left to right: perfect surface, (100) step-edge, ad-row, and ad-atom.

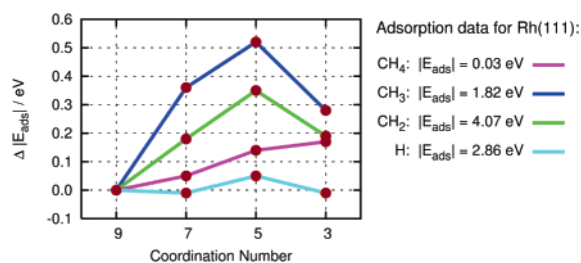


Figure 2. Adsorption energies of methane ( $\text{CH}_4$ ), methyl ( $\text{CH}_3$ ), methylene ( $\text{CH}_2$ ), and atomic hydrogen (H) on a step edge ( $N_C = 7$ ), ad-row ( $N_C = 5$ ), and ad-atom ( $N_C = 3$ ) with respect to the Rh(111) facet ( $N_C = 9$ ).

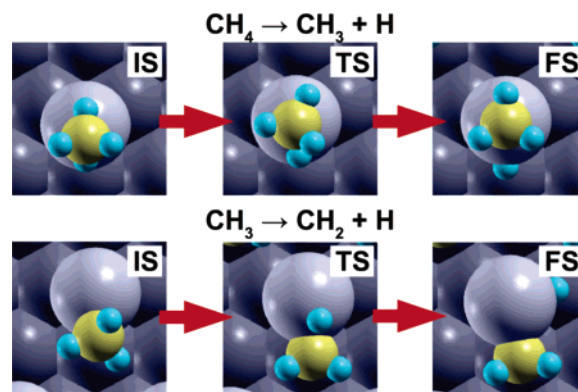


Figure 3. Initial- (IS), transition- (TS), and final-state (FS) structures for the first two steps of methane dehydrogenation over the ad-atom reaction site.

weakly bound to the surface. The reaction begins with the molecule approaching the surface, and then the C–H bond that is closest to the surface starts to elongate. At the TS, the H fragment is located between the bridge and hollow sites, while the  $\text{CH}_3$  fragment is near the top site. The C–H distance at the TS is 1.60 Å (to be compared with an equilibrium value of 1.10 Å), and the activation energy is  $E^* = 0.69$  eV, in good agreement with result of Lui and Hu.<sup>6</sup>  $E^*$  decreases with the coordination of the metal binding site. The reaction at a step edge displays similar features as that at an added row:  $\text{CH}_4$ , initially located on a top site, moves so as to orient the bottom-most H atom toward the bridge site, while the C–H bond is elongated. At the TS, the H fragment is located close

<sup>†</sup> SISSA - DEMOCRITOS.

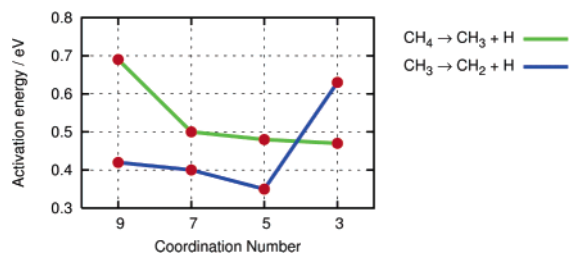
<sup>#</sup> J. Stefan Institute.

to the bridge site, with the CH<sub>3</sub> fragment near the top site. The process is then completed by diffusion of the CH<sub>3</sub> fragment to an adjacent bridge site. Our calculated reaction barriers are 0.50 and 0.48 eV for the step and added row, respectively. All these values are referred to an adsorbed methane molecule in the initial state. In the case of the reaction occurring at a step, correcting this value with the methane adsorption energy would lead to a barrier of 0.42 eV, referred to methane in the gas-phase, to be compared with a value of 0.32 eV calculated by Lui and Hu. At an ad-atom defect, the C–H cleavage of CH<sub>4</sub> starts with a simultaneous elongation of the bottom-most C–H bond and a small rotation of the CH<sub>3</sub> fragment. At the TS state, the CH<sub>3</sub> fragment is located on top of the ad-atom (see Figure 3). The C–H bond is elongated to 1.62 Å. The distance between H and the ad-atom is 1.59 Å, while the distance from H to the nearest surface atom is much longer (2.96 Å). The dissociation then proceeds with the diffusion of the H toward the bridge site connecting the ad-atom with the surface.

As for methyl dissociation, the preferred adsorption site of CH<sub>3</sub> on the flat surface is an fcc hollow site, with the H atoms pointing toward adjacent top sites. The dissociation starts with the displacement of the methyl radical toward a bridge site. At the TS, the detaching H atom is located over the top site (with a bond length of 1.67 Å to be compared with an equilibrium value of 1.09 Å), while the methylene fragment is at the bridge position. The activation energy of 0.42 eV is smaller than that for the first dehydrogenation of methane, as expected from a similar behavior occurring on Ni(111),<sup>7</sup> Ru(0001),<sup>8</sup> and Pd(100).<sup>9</sup>

The dehydrogenation of the methyl radical displays similar features on the step edge and ad-row defects. In the initial state, CH<sub>3</sub> is located asymmetrically between a top and a bridge site at the step (ad-row), with an H atom pointing toward the farthest step-edge Rh atom. During the reaction, the molecule moves toward a bridge site, and then the C–H bond parallel to the step starts to elongate. At the TS, the detaching H atom is on top of a step atom, with a C–H bond length of 1.70 Å. The reaction is then completed by the diffusion of the H atom toward the nearest step-edge bridge site. The activation energy for CH<sub>3</sub> dehydrogenation is only marginally reduced when going from the perfect surface to a step-edge or an added row (from 0.42 to 0.40 and 0.35 eV, respectively). Therefore, the difference in the activation energies of the CH<sub>4</sub> → CH<sub>3</sub> and CH<sub>3</sub> → CH<sub>2</sub> reactions is somewhat smaller at the step edge (ad-row) defective sites.

Let us now come to the dehydrogenation of methyl at an ad-atom defect, which, according to the present study, displays rather unique features (see the bottom panels of Figure 3). To couple the two unpaired electrons of the methylene diradical, CH<sub>2</sub> has to form (at least) two bonds with the substrate. The local structure of an ad-atom defect, however, is such that this requirement is not easily fulfilled. This reaction is initiated by the displacement of the methyl radical from the top of the ad-atom toward an ad-atom-to-surface bridge site, so as to come into closer contact with the surface. Then the uppermost H atom starts to dissociate by going across the ad-atom to the adjacent ad-atom-to-surface bridge site (at the TS, the C–H bond length is 1.63 Å). In the FS, the CH<sub>2</sub> fragment bridges the ad-atom to a surface atom underneath, thus forming two bonds. This rather complicated dissociation path, which is the most favorable among all those that we have been able to identify, has unusually high activation energy (0.63 eV), considerably larger than the one corresponding to the first dehydrogenation of methane. The



**Figure 4.** Activation energies for the first two steps of methane dehydrogenation over a perfect surface ( $N_c = 9$ ), step-edge ( $N_c = 7$ ), ad-row ( $N_c = 5$ ), and ad-atom ( $N_c = 3$ ).

trend of the activation energies for the two reactions is displayed in Figure 4.

Our results indicate that, if it were possible to let the dissociation occur selectively at ad-atom defects, the reaction would be easily blocked after the first dehydrogenation step, provided that methyl does not diffuse away from the ad-atom and further dissociate even more easily on flat facets ( $E^* \approx 0.4$  eV). We predict that the barrier for the methyl diffusion from the ad-atom is rather high ( $E^* \approx 0.6$  eV) and comparable with its local dissociation barrier. In a recent work, Zhang and Hu<sup>10</sup> predicted that the barrier for methane dehydrogenation occurring near an isolated Pt ad-atom on MoO<sub>3</sub>-(010) surface is significantly lower than that on a Pt(111) surface, while the further dehydrogenation of methyl is blocked. We find a similar behavior for Rh ad-atoms on nonreactive metal surfaces, such as copper. Of course, the problem is open on how to fabricate such nanostructured catalysts and how to stabilize them against ad-atom clustering or diffusion in the bulk.

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**Supporting Information Available:** Technical details about the computational method. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) The formation energies of these defects are reported in the Supporting Information. Steps naturally arise at the edge of metal nanoparticles. We do not expect that the formation energy of the ad-atom defects on a facet of a nanoparticle is substantially different from that on a perfect surface.
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