Structure sensitivity of CO dissociation on Rh surfaces

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Using periodic self-consistent density functional calculations it is shown that the barrier for CO dissociation is ~120 kJ/mol lower on the stepped Rh(211) surface than on the close-packed Rh(111) surface. The stepped surface binds molecular CO and the dissociation products more strongly than the flat surface, but the effect is considerably weaker than the effect of surface structure on the dissociation barrier. Our findings are compared with available experimental data, and the consequences for CO activation in methanation and Fischer–Tropsch reactions are discussed.

KEY WORDS: density functional theory; CO adsorption; CO dissociation; steps; methanation; Fischer–Tropsch synthesis; rhodium catalysis; structure sensitivity.

There is increasing evidence, theoretical as well as experimental, that certain defects on transition metal surfaces are extremely reactive compared with flat surfaces [1–3]. Both N_2 and NO dissociation have recently been shown to have barriers for dissociation, which are more than 100 kJ/mol lower at a step than on the most close-packed surfaces of Ru, Fe, Mo or Pd. While it has been known for decades that steps may be more reactive than facets [4,5], it is new that the effect is so large. The magnitude of this effect is such that it makes even measuring the reactivity of the facets extremely hard. A 100 kJ/mol difference in the activation energy leads to a difference of nine orders of magnitude in the dissociation rate at 600 K, whereas even the best-prepared single crystal surfaces have of the order of 1% defects. The order of magnitude of the differences in the dissociation barriers has been determined primarily from density functional theory (DFT) calculations, but for the N_2/Ru system they have also been confirmed by detailed experiments, where the step sites have been selectively poisoned [1,6]. A difference in reactivity of this order of magnitude also means that it must be special step-like configurations on nanoparticle catalysts that are the active sites.

In the present letter we address the question of whether a high reactivity of steps may be found for other molecules and other metals. We consider here CO dissociation on Rh(111) and the stepped Rh(211) surface. Based on extensive DFT calculations we show that the energy of the transition state for CO dissociation at the step is ~120 kJ/mol lower than on the terrace. We further show that the results of the calculation are in good qualitative agreement with detailed experiments on Rh single crystal surfaces and on supported nanoparticles.

CO dissociation is an important first step in both the methanation reaction and in Fischer–Tropsch synthesis [7,8]. These reactions take place over a number of transition metals. We have chosen to focus here on Rh surfaces, because there are very detailed experimental data for CO dissociation on flat [9] and stepped surfaces [10,11] as well as on small Rh particles of varying size [12–14]. This allows us to discuss our theoretical findings in the light of these experiments.

In the density functional calculations the Rh(111) surface is modeled by a three-layer slab repeated periodically with a (2×2) unit cell parallel to the surface. The Rh(211) surface is similarly modelled by a nine-layer slab and a (2×3) surface unit cell. Five (or 14) equivalent layers of vacuum were used to separate any two successive metal (111) (or (211)) slabs. The calculations are based on an expansion of the wave functions in plane waves and on the description of the ionic cores by non-local ultra-soft pseudopotentials [15]. Plane waves with kinetic energies up to 25 Ry and 18 special k points (or 16 k points) have been used to sample the first Brillouin zone of the (111) (or (211)) surface. Exchange and correlation effects are described within the generalized gradient approximation [16]. The self-consistent electron density is determined using the PW91 exchange-correlation functional by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density. All total energies have been extrapolated to $k_B T = 0$ eV. The structures and electron density have then been used to calculate the interaction energies using the more accurate RPBE functional [17]. The use

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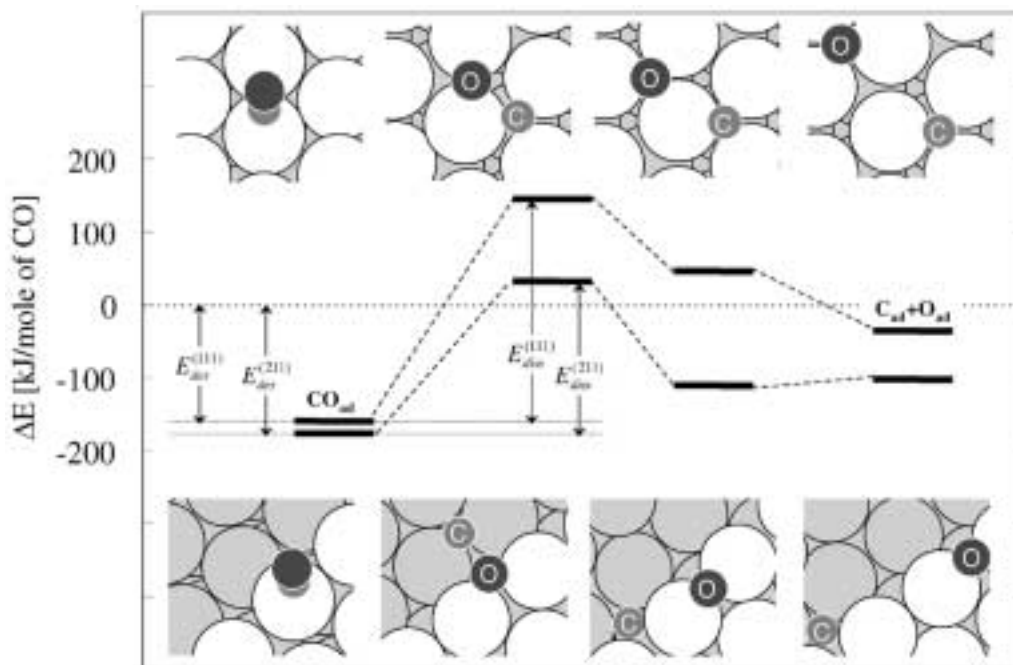* To whom correspondence should be addressed.

Figure 1. One-dimensional potential energy diagram for CO dissociation on Rh(111) and Rh(211) surfaces. E_{diss} and E_{des} represent the activation energies for dissociation and desorption with respect to the molecularly adsorbed state (CO$_{ad}$). The top set of panels gives snapshots from the CO dissociation path on Rh(111), whereas the bottom set of panels gives the corresponding snapshots from the CO dissociation path on Rh(211). The first snapshot of each panel represents the corresponding molecularly adsorbed state, the second snapshot represents the transition state, the third snapshot represents an "immediate" dissociated state (C$_{ad}$ + O$_{ad}$), and the fourth snapshot represents the final dissociated state, after diffusion of the dissociation products away from their original adsorption sites has occurred.

of the non-self-consistent electron densities introduces a negligible error due to the variational principle [17]. Adsorption is allowed on only one of the two surfaces exposed and the electrostatic potential is adjusted accordingly [18]. For adsorbed CO, C and O, additional test calculations performed with up to, for instance, six metal layers for the (111) slab show that the results presented here remain practically invariant with the number of metal layers used. For each configuration all degrees of freedom for CO and the topmost Rh layers (one for the (111) slab and four for the (211) slab, respectively) have been allowed to relax. The reaction paths have been found by varying the CO bond length and relaxing all other degrees of freedom for each configuration. We know from calculations for similar molecules dissociating on similar surfaces [2,3,19] that the reaction path is essentially parallel to the C–O bond length around the transition state, so this procedure should be adequate for locating the transition state.

The results are summarized in figure 1, showing the one-dimensional energy landscape for the dissociation of CO on Rh(111) and Rh(211). The calculated equilibrium structures of the initial and final states as well as the transition state structures are also shown in figure 1. CO adsorbing at a step is clearly more stable than on the terrace. We found that CO adsorbs on top of an Rh atom, both on the (111) and on the step edge of the (211) surface, for a total coverage of 1/4 ML and 1/6 ML, respec-

tively. This is in excellent agreement with the available experimental evidence for CO adsorption on a Rh(111) surface [20]. When we compare atop CO on the (111) surface and at the step, the local adsorption geometries are very similar, but still the CO is ~15 kJ/mol more stable at the step. We associate this with the fact that the Rh d electrons are higher in energy and thus interact more strongly with the CO valence states, just as for CO and N$_2$ adsorption on Pt steps [21–23]. Similar results indicating that O$_2$ and CO bind more strongly at the step-edges of Au surfaces have been reported recently [24]. We have also found that CO can fully saturate the step-edge of Rh(211) without substantial loss of the binding strength per CO molecule (~15 kJ/mol decrease in binding energy between 1/6 ML and 1/3 ML coverages). However, when the step edge of Rh(211) is fully saturated, CO clearly prefers the bridge sites between successive Rh edge atoms, not the top sites.

When it comes to the final state of the dissociation reaction, adsorbed C and O atoms are also considerably more stable at the step than on the (111) surface. The energy shown is for the case where the C atom and the O atom are close (figure 1, column 3) and far apart from each other (figure 1, column 4). The structures drawn in figure 1 suggest that C prefers a highly coordinated site at the bottom of the step edge, whereas O prefers a two-fold coordinated site at the step-edge itself.

The largest effect of the step on the energetics is for the dissociation barrier. There are two reasons for this. One is that the step atoms are more reactive, as observed for *e.g.* the molecularly adsorbed state. The other reason is related to the fact that a special transition state geometry exists at the step-edge, which is not available on the (111) surface (figure 1). At the step, the CO–surface inter-action at the transition state involves five Rh atoms rather than four for the transition state at the (111) surface. This gives a substantially stronger interaction, since the C and the O atoms do not have to share metal atoms [2,3,25].

Detailed experiments have shown that CO cannot dissociate on Rh(111) [9], but there are reports for CO dissociation in connection with steps and other defects [10,11]. This agrees well with our calculated results. If CO is first adsorbed and the system is subsequently heated up, the fraction, f, of the molecules dissociating at a given temperature, T, will be given approximately by

$$f = \frac{v_{\mathrm{diss}}\, e^{-E_{\mathrm{diss}}/kT}}{v_{\mathrm{diss}}\, e^{-E_{\mathrm{diss}}/kT} + v_{\mathrm{des}}\, e^{-E_{\mathrm{des}}/kT}}$$

where v_{diss} and v_{des} are attempt frequencies in the rate expression for dissociation and desorption, respectively, and E_{diss} and E_{des} are the corresponding activation energies (figure 1). If $E_{\mathrm{diss}} - E_{\mathrm{des}} \gg kT$ and if the attempt frequencies for the two processes are not much different, then $f \approx (v_{\mathrm{diss}}/v_{\mathrm{des}})\, e^{-(E_{\mathrm{diss}}-E_{\mathrm{des}})/kT}$ is given essentially by the energy difference $E_{\mathrm{diss}} - E_{\mathrm{des}}$, which is the energy of the dissociation transition state relative to vacuum. Clearly our calculated barrier for the terrace will give an extremely small value for f, even when the inherent inaccuracy of the DFT calculations ($\sim$0.2 eV [17]) is taken into account. At the step, on the other hand, $E_{\mathrm{diss}} - E_{\mathrm{des}} \approx 0.3$ eV and some dissociation should be possible. Within our accuracy, it is therefore not unreasonable that f should be of the order 0.1 at $\sim$450 K as observed experimentally for the Rh(210) surface [11].

We note that other defects may be even more reactive. Metal atoms at kinks, for instance, have a lower metal coordination number than step atoms on the (211) surface (6 rather than 7). They therefore have even higher-lying d bands and should be even more reactive. This has been shown clearly for CO bonding to steps and kinks on Pt(111) [21,22].

We conclude that our calculations are in good qualita-tive agreement with experimental findings that the (111) surface cannot dissociate CO, while steps and other defects may be able to break the C–O bond. It is also clear that CO dissociation belongs to the class of reactions that are extremely *structure sensitive*—in fact so sensitive that reaction on the close-packed surfaces is virtually impossible under most conditions. Such reactions can end up appearing almost structure-

insensitive simply because the reaction is dominated by defects on all low-index surfaces as well as on small-particle catalyst particles. It will, therefore, be the same kinds of site that give rise to the measured activity no matter which surface is studied, and if the concentration of defects is about the same, and the reaction barrier is about the same for the defects, the reaction will appear structure-insensitive.

The fact that the adsorbed C and O bind strongly to the step indicates that during a low-temperature adsorp-tion experiment the products will poison the active sites and the reaction should stop when all step sites are occupied. This has indeed been observed experimentally for alumina-supported Rh particles; after dissociating CO, pre-adsorbed at 90 K, by heating to 600 K, no further accumulation of carbon could be detected in subsequent adsorption and annealing cycles [26]. During a full catalytic reaction the situation will be different, though. If H_2 is provided together with CO, the adsorbed C and O can be hydrogenated away, and new free sites appear. If, for instance, methane formation from adsorbed C and H is also facilitated by steps, steps may be the preferred sites for the methanation reaction, too. Under all circumstances, we note that because the lowering of the transition state energy is substantially larger than the step stabilization of the reaction products, the steps should dominate the reaction, if it proceeds at all. The reason is that the sum of the energy it costs to move the products away from the steps and the activation energy for CO dissociation at the step is considerably smaller than the barrier for CO dissociation on the terraces.

The dissociation of CO on small Rh particles as a function of particle size has been studied in great detail [12–14]. Rh particles supported on thin alumina films are found to show a dissociation fraction f which has a maximum for particles containing about 150 Rh atoms (figure 2). The maximum value of f approaches 0.5 and f levels off around 0.3 at higher particle sizes. In accord with the single-crystal studies, it has been sug-gested that steps and other defects are responsible for the dissociation activity of the small particles [12–14], and the calculated results in figure 1 fully support this view.

The picture we arrive at is therefore one where the catalytic activity of the supported Rh nanoparticles is related to the large number of defects that are present at the surface of such small particles. We note in this connection that since both CO and, not least, the reaction products, adsorbed C and O, interact very strongly with steps, such defects may actually be created during the process. According to our calculations the energy required to form a step atom on the clean surface is of the order 25 kJ/mol of step atoms as compared to an extra step bonding of CO and C + O of 15 and 70 kJ/mol, respectively. A static view of the surface is therefore not possible during a catalytic reaction.
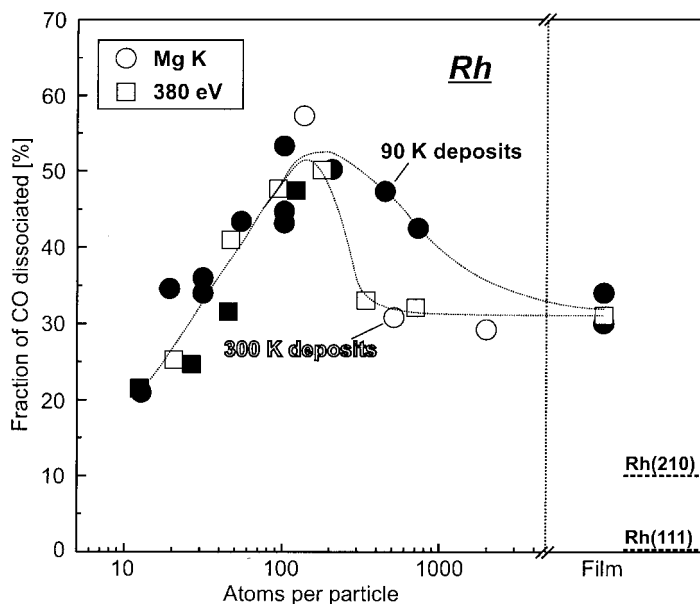
Figure 2. CO dissociation activity on Rh particles grown at 90 K and at 300 K as determined by XPS. For comparison, the activity observed on selected Rh single-crystal surfaces is indicated as well [9,11].

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