Any technologically important chemical reaction typically involves a number of different elementary reaction steps consisting of bond-breaking and bond-making processes. Usually, one assumes that such complex chemical reactions occur in a step-wise fashion where one single bond is made or broken at a time. Using first-principles calculations based on density functional theory we show that the barriers of rate-limiting steps for technologically relevant surface reactions are significantly reduced if concerted reaction mechanisms are taken into account.

1. Introduction

Chemical reactions at surfaces are of outstanding technological importance since they correspond to the basic processes occurring in heterogeneous catalysis, corrosion, sensing, and so forth. They also play a crucial role in energy storage and energy conversion in renewable energy systems. Hence, an understanding of the basic mechanisms occurring in surface reactions is not only interesting from a fundamental point of view, it is also beneficial from a technological point of view. Modeling such surface reactions, one usually assumes that the reaction steps involving bond-breaking and bond-making processes occur in a consecutive fashion (see, e.g. [2]).

However, it is well known that chemical reactions can also proceed in a concerted fashion, which means that bond breaking and bond making occur simultaneously, for example, in the so-called S_n2 reaction. Yet, there are usually severe symmetry constraints involved in concerted reaction mechanisms, such as those expressed in the Woodward–Hoffman rules, which state that the symmetry of the wave function shall remain unchanged upon this reaction.

On the other hand, configurations in surface reactions often exhibit little symmetry which is also true for the involved electronic states. Herein, using first-principles calculations based on density functional theory (DFT) we show that the barriers of rate-limiting steps for technologically relevant surface reactions are significantly reduced if concerted reaction mechanisms are taken into account. We illustrate this using the reaction paths of two technologically relevant reactions as examples, namely methanol synthesis on copper and subsurface penetration of hydrogen on palladium. In fact, these reactions are of high relevance for our understanding of elementary processes in chemical energy storage and conversion.

Computational Methods

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP). Exchange-correlation effects were described within the framework of the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional. Ionic cores were represented by projector-augmented wave (PAW) potentials as constructed by Kresse and Joubert. Metal substrates were represented by four- and five-layer slabs. Integration over the first Brillouin zone in reciprocal space was replaced by a sum over a sufficiently large set of k-points. Reaction barriers were evaluated by using the reversible-work transition-state theory (rwTST) which was implemented into the VASP by Jonsson et al. In practice, we used the nudged elastic-band (NEB) method to find the minimum energy paths and activation barriers.

2. Methanol Synthesis

Methanol synthesis is of significant importance because it is the basis for many chemicals. Furthermore, methanol is considered as a potential fuel in the hydrogen technology. Industrially, methanol is produced by the hydrogenation of carbon dioxide, which results from the preceding water-gas shift reaction of natural gas on oxide-supported Cu/ZnO catalysts. Interestingly, the exact reaction mechanism leading to the formation of methanol is still debated in spite of the importance of this reaction. Since it is assumed that metallic Cu particles rather than ZnO are the active material in methanol synthesis, several surface-science studies have been performed on Cu single-crystal surfaces, in order to elucidate the reaction mechanism in methanol synthesis and in the reverse process, oxidation of methanol. Herein, we concentrate on the Cu(110) surface which represents a model system for the interaction of methanol with Cu.

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Experiments indicate that CO$_2$ is the primary source in methanol production. Therefore, in our computational study we focused on the reaction path starting at the point where CO$_2$ interacts with the dissociative adsorbed hydrogen on the Cu(110) surface. Note that mechanistic details of the water-gas shift reaction CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$ have been addressed previously in theoretical studies. According to our analysis, the initial reaction steps lead to the formation of adsorbed dioxymethylene on Cu(110) [H$_2$COO$^a$], superscript ($a$) indicates that the molecule is adsorbed on the surface, Figure 1 and 2. In a previous DFT study on Cu(111) lower barriers were found for the formation of formic acid (HCOOH) from formate ($E_a$ = 0.91 eV) than for the formation of desoxymethylene ($E_a$ = 1.59 eV). However, on Cu(110) the barrier for desoxymethylene formation is much lower ($E_a$ = 0.95 eV). Furthermore, isotopic-labeling studies showed that methanol cannot be synthesized by HCOOH hydrogenation. Hence we focused on the reaction pathway involving desoxymethylene as a reaction intermediate.

As for the subsequent reaction mechanism, assuming a step-wise mechanism involving a CO-bond breaking followed by a hydrogenation step leads to the following reaction scenario:

\[
\begin{align*}
H_2COO(a) + H^a &\rightarrow CH_2O(a) + OH(a) \\
CH_2O(a) + H^a &\rightarrow CH_3O(a)
\end{align*}
\]

However, the first reaction step (1) on Cu(110) is hindered by a significant barrier of 1.8 eV according to our calculations. Some time ago it has been proposed that the methanol synthesis on Cu might involve a reaction step

\[
H_2COO(a) + H^a \rightarrow CH_3O(a) + O(a)
\]

that corresponds to a combination of C–O-bond scission and hydrogenation. This reaction step was proposed purely because of kinetic reasons in order to reproduce the experimentally observed reaction order, but no mechanistic model in terms of a microscopic reaction mechanism was given. In a recent DFT study on methanol synthesis on Cu(111), however, such a concerted mechanism could not be identified. Yet, based on a comparison of DFT results with binding energies derived from microkinetic modeling, the authors concluded that Cu(111) might not provide a suitable representation of the active site for methanol synthesis. It might also well be that the proper initial configuration of the co-adsorbates on the surface has been missed.

Using the nudged elastic-band (NEB) method, an unbiased automatic transition-state search routine, we looked for the most favorable reaction path connecting the initial state of dioxymethylene in the presence of adsorbed hydrogen atoms (Figure 1). As a first step, we carefully determined the energetically most favorable configuration of the hydrogen atoms in the vicinity of the adsorbed dioxymethylene molecule. Along the reaction path, first, the dioxymethylene molecule is reoriented and one oxygen atom of the molecule moves from a two-fold bridge-like site towards a quasi-threefold hollow site on the Cu(110) surface. The corresponding distortion of the molecule is associated with a large energy cost of more than 1 eV. Before the transition state, there is a plateau in the potential energy which, however, does not correspond to an intermediate state. At the transition state, one C–O bond is already significantly elongated and the CH$_2$ group starts to rotate. While the one C–O bond is further elongated, a hydrogen atom from the Cu surface is forming a C–H bond, thus turning the evolving formaldehyde (CH$_2$O) into a methoxy radical (CH$_3$O). The energy of the transition state is about 1.4 eV, that is 0.4 eV lower than the barrier for the mechanism involving two consecutive reaction steps. Note that such a reduction in the barrier height leads to an increase in the rate constant by more than 2–3 orders of magnitude at 600–900 K, the temperature range in which methanol is typically synthesized.

In order to determine the electronic factors underlying this reduction in the barrier height, we analyzed the local density of states (LDOS) of the reacting complex along the reaction...
path for the concerted reaction (3) (Figure 2). At the transition state, where the C–O bond is already significantly extended, there is a strong rearrangement of the electronic states with an anti-bonding π* orbital of CO appearing just above the Fermi energy, whereas the electronic distribution just before and after the transition state look rather alike. In the framework of the frontier-orbital concept of Fukui, the lowest unoccupied molecular orbital (LUMO) close to the Fermi energy at the transition state leads to a rather reactive complex. One can also put it differently, directly after the C–O bond breaking the missing bonding partner O is replaced by the nearest hydrogen atom resulting in an equivalent coordination situation of the carbon atom.

It is important to note that another consequence of this concerted reaction mechanism is that the formation of formaldehyde (CH₂O) is avoided. Being a volatile product and only weakly bound to Cu at the temperature methanol is synthesized, it would immediately desorb under these reaction conditions. It also means that the methanol synthesis would remain incomplete if formaldehyde was formed. Furthermore, this rationalizes why formaldehyde cannot be produced industrially through the oxidation of CO or CO₂, but is rather formed through the partial oxidation of methanol.

The final step after the methoxy formation is the recombination of methanol and water, which is hindered by a relatively small barrier of 0.5 eV. The calculated overall reaction for methanol synthesis on H-covered Cu(110) is summarized in Figure 3. It becomes apparent that the conversion of adsorbed dioxymethylene has the highest barrier of all the reaction steps involved. This means that it corresponds to the rate-limiting step, which is significantly lowered by taking the concerted reaction mechanism into account.

Interestingly, in the electrochemical reduction of CO₂ at Cu electrodes methane rather than methanol has been observed as a reaction product. Recently it has been suggested that this might be due to the fact that in heterogeneous catalysis the hydrogen atoms used for hydrogen addition are coadsorbed hydrogen atoms, whereas in electrocatalysis the protons are delivered by the solvent. Therefore an entirely different reaction mechanism is operative.

3. Hydrogen Subsurface Penetration

As a second example, we considered the subsurface penetration of hydrogen on Pd(100). Currently, there has been a renewed interest in the hydrogen absorption in metals in the context of the hydrogen technology. Due to its high specific mass, Pd is no longer considered as a candidate material for hydrogen storage. Still, it is considered to be the model system for hydrogen-absorption studies. Furthermore, thin capping palladium films are typically used as hydrogen-insertion promoters for complex hydrides formed by light elements. In addition, subsurface penetration of hydrogen in Pd nanoparticles might be the crucial promoter for olefin hydrogenation.

According to experiments, hydrogen first adsorbs on the Pd surface before bulk absorption starts. Only after the surface is covered by hydrogen, subsurface penetration occurs, but then rather easily. This is in variance with the accepted notion that hydrogen penetration into the Pd bulk is hindered by barriers of considerable height. Therefore, it is of interest whether the high barrier for H subsurface penetration is influenced by the presence of hydrogen adsorbates through, for example, a defect-mediated or a concerted reaction mechanism.

Static DFT calculations confirmed the preferential occupation of adsorption sites on the surface by demonstrating that hydrogen subsurface absorption is energetically less favorable than adsorption on the surface. Since possible concerted reaction mechanisms are sensitive to the initial configuration, ab initio molecular dynamics (AIMD) simulations of the H₂ dissociative adsorption on hydrogen-precovered Pd(100) were employed for an unbiased search of concerted reactions for varying hydrogen coverages.

Besides hydrogen adsorption and diffusion on the surface, another event was frequently observed in the AIMD simulations, namely the subsurface penetration of a hydrogen atom involving another hydrogen atom at an adjacent bridge site in a concerted fashion. Snapshots of this process on a hydrogen-covered Pd(100) surface with an initial coverage of θ₈ = 0.5 monolayer within a (3×2) unit cell are shown in Figure 4 (top and side view, the animated process is provided in the Supporting Information as Movie S1). Note that the coverage is defined with respect to the number of Pd atoms in the surface. Figure 4a shows five hydrogen atoms per unit cell, four of them adsorbed at four-fold hollow sites and one hydrogen atom adsorbed at a bridge site (labeled number 2), which is surrounded by filled four-fold hollow sites. In Figure 4b the central H atom (labeled number 1) at one of the four-fold hollow sites starts to propagate towards a subsurface site and hydrogen atom 2 from the adjacent bridge site moves towards the four-fold hollow site that is about to be emptied. Thus, the penetration can be described as a combined bond-making/bond-breaking process, where a hydrogen atom enters the subsurface site, while its four-fold hollow site is immediately refilled by the hydrogen atom from a nearby bridge site (Figure 4c).
In order to analyze these observations, reaction paths for the hydrogen subsurface penetration were determined using the NEB method again.\[10\] The results are summarized in Figure 5. We started with a \(c(2\times2)H/Pd(100)\) surface as initial configuration, that is, with a surface with a hydrogen coverage of \(\theta_H = 0.5\), but with no adjacent hydrogen vacancies so that \(H_2\) cannot dissociate directly.\[37\] Above the Pd ontop site, there is a molecular adsorption state on the surface denoted by \(H_2,ad\) (Figure 5) which is stabilized by a rearrangement of the adjacent substrate atoms. The dissociation of \(H_2\) into two next-nearest neighbor sites from this state is hindered by a barrier of about 0.3 eV (dashed red line in Figure 5). At the fully hydrogen-covered Pd(100) surface, the subsurface penetration of a single hydrogen atom is hindered by a barrier of about 0.6 eV. This high barrier is due to the fact that the hydrogen atom has to propagate through a low-coordinated transition state also involving strain effects. Note that the situation with a barrier of only about 60 meV. In contrast, the propagation of the \(H_p\) atom into an empty four-fold hollow adsorption site is much less probable and is hindered by a barrier of more than 0.2 eV.

In the concerted motion, the energy cost of the \(H\) atom going through the low-coordinated transition state towards the subsurface site is compensated to a large extent by the energy gain when the bridge-site hydrogen atom enters the four-fold hollow site that is about to be emptied. The combined effects result in a concerted process that is hindered by a barrier of less than 0.1 eV. Similar results were found for an initial hydrogen coverage of \(\theta_H = 0.75\) (see the Supplementary Information Figure S2 and Movie S2). Such a concerted motion provides an explanation for the facile hydrogen subsurface penetration once the surface is almost covered with hydrogen.\[33\] This also indicates that there is no need to invoke any defect-mediated mechanisms in order to explain the facile subsurface penetration.\[34\]

4. Conclusions

We demonstrated, based on periodic DFT calculations, that concerted reaction mechanisms can be a crucial part of technologically relevant reactions on surfaces. The driving force for these concerted reaction mechanisms is given by the fact that it is energetically favorable to create a new bond before the preceding bond-breaking process is fully completed, which is not hindered by symmetry selection rules at surfaces. Other concerted reaction mechanisms in surface reactions have been identified before, for example in the oxidation of methanol.\[39, 40\] On the other hand, sometimes concerted mechanisms could not be found in spite of significant efforts in exploring the relevant potential energy landscape.\[20\] However, it is important to note that a prerequisite for the occurrence of a concerted reaction mechanism is the availability of a second reaction partner. Hence, either a careful search for appropriate ini-
tial configuration is required, or an unbiased search using, for example, AIMD simulations\cite{26,41} has to be performed. Without the proper initial configuration, there is no chance to identify concerted reaction mechanism which could have lower reaction barriers. It might well be that the most favorable reaction mechanism has often been missed in computational studies. This is the reason why we believe that concerted reaction mechanisms are much more common than previously assumed.

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