Electronic Effects in the Activation of Supported Metal Clusters: Density Functional Theory Study of H$_2$ Dissociation on Cu/SiO$_2$

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We have performed density functional theory calculations on the dissociation of molecular hydrogen on small gas-phase and silica-supported Cu clusters and on the Cu(111) surface. The Cu surface and the silica support have been represented by cluster models. The supported Cu clusters interact with a nonbridging oxygen, a paramagnetic defect present on the surface of dehydroxylated silica, giving rise to a partial charge transfer to the substrate. While free Cu clusters and the Cu metal are rather unreactive toward H$_2$ dissociative adsorption, the supported clusters exhibit a much higher reactivity connected with a strong geometrical rearrangement of the metal structure. As a consequence of the interaction with the substrate, the Cu clusters become active catalysts in H$_2$ dissociation.

1. Introduction

Supported metals are of fundamental importance in industrial catalysis because of the modification of the metal properties induced by deposition, and of the high dispersion and high surface area of the supported catalyst.[1] Metal-supported catalysts consist of 1−10 nm metal particles deposited on oxide substrates. For small particles, significant variations of the metal properties may occur, especially for particle sizes smaller than 5 nm. In these systems the number of atoms in low-coordinated positions is greater than 10% of the total.[2] The size effect is one of the key points in the reactivity of supported metal catalysts. For this reason the study of metal−support interactions with surface science techniques has attracted great interest in the last years.[2−4] Recently, mass-selected metal clusters of size ranging from one to a few tens of atoms have been deposited at low temperature by a soft landing technique on the surface of MgO thin films.[5] The reactivity of the supported Ni, Pt, and Pd clusters toward CO oxidation and dissociation or acetylene trimerization have been studied as a function of cluster size.[5−7] These studies open new perspectives for the detailed understanding of size and shape dependence of the catalytic activity. Two main factors are included in the so-called "size effect". The first one is a purely electronic effect caused by the modification of the density of states of the supported particle compared to the bare metal. It can include contributions originated by the interaction of the particle with the support but also the modifications of the electron density due to the small dimensions of the particle. The second factor is of geometrical type and involves the stabilization of shapes showing unusual faces or sites on the surface of the aggregates. For nanometer size particles these two contributions have been studied in terms of equilibrium static conditions but the role of

the size effect in the reactivity of the supported metal is far from being understood.

One of the reactions that have been studied in more detail experimentally and theoretically is the dissociation of molecular hydrogen on transition metal surfaces.[8−16] This is one of the elementary steps in the methanol synthesis and in the hydrogenation of unsaturated hydrocarbons. One of the characteristic features of the hydrogen adsorption on Cu surfaces is the presence of a barrier for dissociative adsorption.[16] This behavior is caused by the full d band of the Cu metal. However, the various crystallographic faces, (111), (110), or (100), exhibit quite different reactivities and can also be rather inert.[17] Adsorption of H$_2$ on copper aggregates supported on SiO$_2$ has also been studied by means of TPD.[17] The measured heat of adsorption for relatively high coverage of Cu on SiO$_2$ is not too different from what has been measured on Cu powders, thin films, or stepped Cu single crystal surfaces.[17] This shows that large Cu aggregates deposited on silica behave more or less as a stepped surface. On the other hand, gas-phase, mass-selected Cu clusters are completely unreactive toward molecular hydrogen.[18] Of course, this is also connected to the fact that the mass-selected Cu clusters are the most stable ones, hence the less reactive. It is possible, in principle, that deposition on "inert" substrates induces changes in the geometrical and electronic structure of the cluster, resulting in a different reactivity toward hydrogen. The aim of the present study is precisely this aspect. To this end we have performed ab initio calculations to copper-based systems toward H$_2$ dissociation.

The microscopic understanding of the geometrical and electronic effects that determine the cluster reactivity, including the role of the support, can highly benefit from the use of theoretical methods. The deposition of metal clusters on oxides is the subject of different studies employing a variety of theoretical approaches.[19−25] However, the deposition of metal
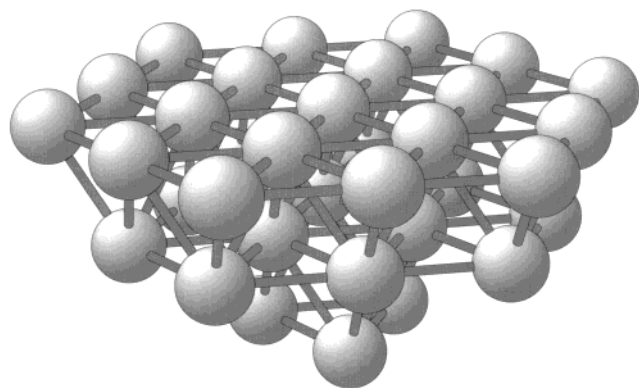

Figure 1. Schematic representation of the Cu$_{34}$ cluster representing the Cu(111) surface.

atoms on SiO$_2$ has been investigated theoretically only recently[26] despite the importance of this system in catalysis. It has been shown that the regular, nondefective sites of the silica surface are quite unreactive toward metal atoms and that strong adhesion occurs only at the defect sites,[26-28] like for instance the nonbridging oxygen, NBO, or the Si dangling bond, two paramagnetic centers present on the surface of dehydroxylated or mechanically activated silica.[29] In particular, the NBO centers are very reactive.[26] In this paper, we describe the geometry and the energetics of the interaction of H$_2$ on small Cu clusters adsorbed on the NBO defective centers of the silica surface. No activation barriers have been computed and the conclusions are based on purely thermodynamic arguments. We will show that the main difference between isolated Cu clusters or the Cu(111) surface and the supported units is that while no evidence of dissociative adsorption has been found on the formers, the supported Cu clusters efficiently activate the H$_2$ dissociation.

2. Computational Approach

The interaction of hydrogen with free and supported Cu clusters and with models of the Cu(111) surface, Figure 1, has been investigated by means of the hybrid B3LYP[30,31] density functional theory, DFT, approach which makes use of gradient-corrected forms of the exchange and correlation functionals and includes nonlocal terms in the exchange part. This method has been chosen because of its good performance in the study of metal—oxide adhesion.[25] Hydrogen dissociation on Cu(111) has proved to be very sensitive to the choice of the functional, LDA being erroneous not only in the description of the energy barrier for dissociation but also in thermochemistry;[16] gradient-corrected functionals are needed to properly describe these features.

The SiO$_2$ substrate or the Cu(111) surface has been represented by finite clusters, Figures 1–5. For the Cu/SiO$_2$ system the model consists of small Cu$_n$ ($n = 3, 5$) clusters adsorbed on the most reactive defective site of the SiO$_2$ surface, the nonbridging oxygen, NBO.[29] This center consists of a broken ≡Si—O• bond and is characterized by the presence of an unpaired electron on the terminal O atom. The cluster employed to describe the NBO center at the SiO$_2$ surface is derived from the structure of α-quartz.[32] The oxygen dangling bonds have been saturated by H atoms placed at 0.98 Å along the direction of the O—Si bonds in α-quartz. The terminal H atoms have been kept fixed in the geometry optimization so as to provide a crude representation of the mechanical embedding of the solid matrix. The local nature of the bonding between the metal and the defect sites of the silica network has been proved previously by means of a combined quantum-mechanical/molecular me-
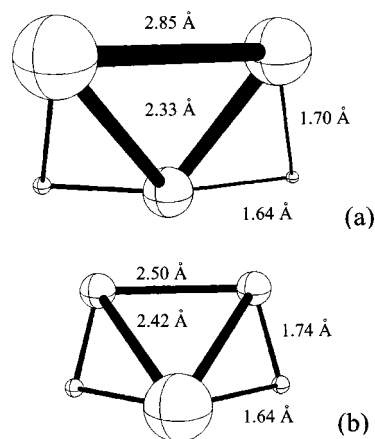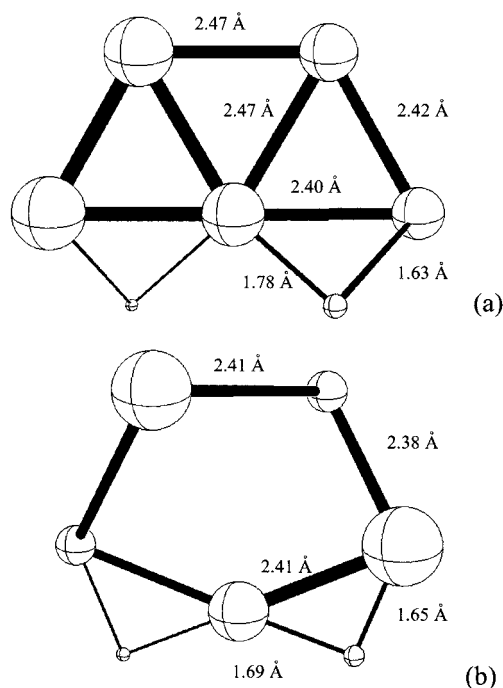

Figure 2. Geometry optimization of H$_2$ adsorbed on gas-phase Cu$_3$: (a) only the position of the H atoms is optimized; (b) full optimization.
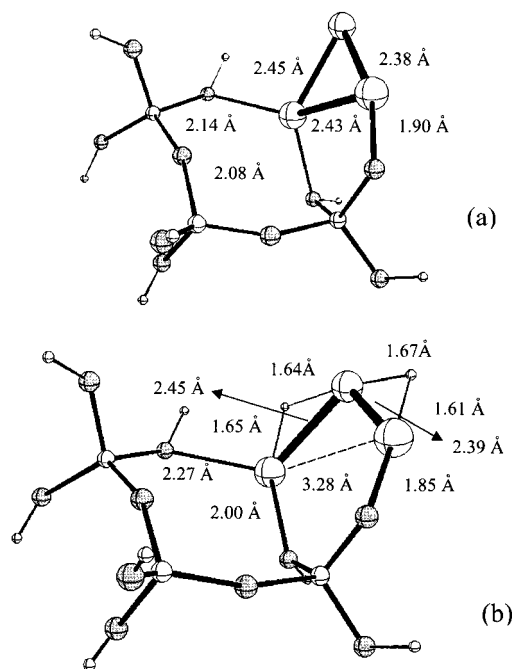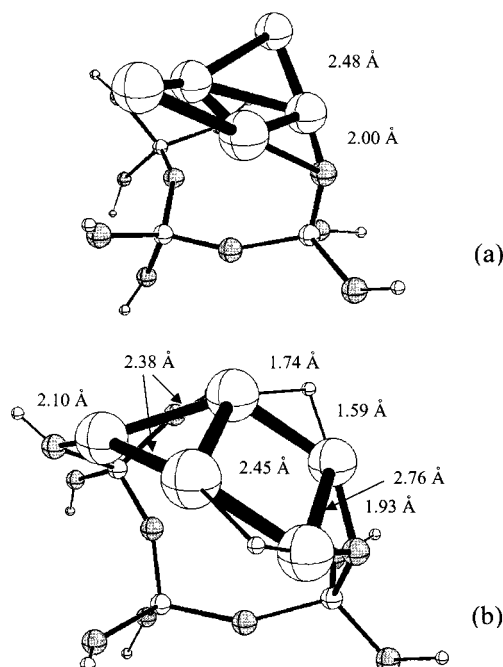

Figure 3. Geometry optimization of H$_2$ adsorbed on Cu$_3$ (larger spheres) supported on a NBO center on the SiO$_2$ surface, ≡Si—O—Cu$_3$; (a) structure of the supported Cu$_3$ cluster; (b) structure of the supported Cu$_3$ + 2H cluster.

chanics approach.[33] The cluster used, a three tetrahedra model, (OH)$_3$Si—O—Si(OH)$_2$—O—Si(OH)$_2$—O•, Figures 3 and 5, is the same employed previously for the adsorption of Cu$_n$ clusters at both NBO[34] and Si dangling bonds[35] defect centers. For comparison, the interaction of hydrogen has been investigated also on small gas-phase Cu$_3$ and Cu$_5$ clusters and on the Cu(111) surface. The cluster model to represent the Cu(111) face contains 34 atoms, 19 in the first, 12 in the second, and 3 in the third layer, respectively, Figure 1.

The basis sets used for the H$_2$ molecule are 6-31G**;[36] Cu atoms have been described by the small core effective core potential, ECP, of Hay and Wadt with a [8s5p4d/3s3p2d] basis set.[37] For the description of the silica support we used a small 3-21G[38] basis set for terminal H atoms and 6-31G*[36] for both oxygen and silicon atoms. In the representation of the Cu(111) surface, the seven atoms that are nearest neighbors to the adsorbed H atoms have been treated with a small core ECP, while the remaining atoms have been represented by a one-electron ECP and a [4s1p/2s1p] basis set.[39]

Figure 4. Geometry optimization of H_2 adsorbed on gas-phase Cu_5: (a) only the position of the H atoms is optimized; (b) full optimization.

Figure 5. Geometry optimization of H_2 adsorbed on Cu_5 (larger spheres) supported on a NBO center on the SiO_2 surface, $\equiv Si-O-Cu_5$: (a) structure of the supported Cu_5 cluster; (b) structure of the supported $Cu_5 + 2H$ cluster.

Geometrical optimizations have been performed in two or three steps for the following systems: (i) Cu(111)−H_2, (ii) Cu_3, Cu_3H_2, (iii) NBO−Cu_3, NBO−Cu_3−H_2, (iv) Cu_5, Cu_5H_2, and (v) NBO−Cu_5, NBO−Cu_5−H_2. In the optimization of H_2 on the Cu(111) surface the position of the metal atoms was kept fixed (no surface relaxation or reconstruction). For H atoms adsorbed on gas-phase Cu clusters two optimizations have been performed. In the first one we fixed the position of the Cu atoms and we allowed only the two H atoms to move; in the second step of the optimization the entire system is free to relax. For H atoms adsorbed on supported Cu clusters three optimizations

TABLE 1: Mulliken Population Analysis for H Atoms Adsorbed on the Cu(111) Surface, on Gas-phase Cu Clusters, and on Cu Clusters Supported on a NBO Center on Silica

	Cu(111)		Cu_3		Cu_5	
	(T) sites	(O) sites	gas phase	supported	gas phase	supported
$Q_{Cu}{}^a$	+0.01	+0.01	+0.06	+0.13	+0.02	+0.04
Q_H	−0.02	−0.01	−0.09	−0.11	−0.04	−0.07
spin			0.90 (Cu)		0.85 (Cu)	
density			0.05 (H)		0.07 (H)	

^{a} Average values. For Cu_{34} only the seven atoms described by a small core ECP are considered.

have been performed: in the first one we relaxed the two H atoms, in the second one the H and the Cu atoms of the cluster were relaxed but not the substrate, and in the third we allowed relaxation of the whole adsorbate/metal/support system (only the terminal H atoms of the SiO_2 cluster were kept fixed).

3. Results and Discussion

3.1. Structures. We consider here the geometric aspects of the H_2 dissociative adsorption process starting with the model of the Cu(111) surface, Figure 1. The adsorption of H_2 on Cu(111) leads to two possible configurations, one with the two H atoms in the tetrahedral sites (T) and one where the octahedral sites (O) are occupied. No subsurface state has been explored since these states become occupied only at high coverage.[40] The optimal Cu−H distances are about 1.78 ± 0.01 Å on both O and T sites; we will see below that these distances are somewhat longer than those found for adsorption on the free and supported clusters.

The adsorption of two H atoms on the Cu_3 and Cu_5 clusters leads to several local minima and it should be kept in mind that the structures found in the present study do not necessarily represent global minima. Although other local minima have been found, we discuss only the most stable structures. Gas-phase Cu_3 has a Jahn−Teller distorted triangular structure with two short and one long Cu−Cu distances. Two H atoms were added in the bridge position above the short Cu−Cu distances, Figure 2a. Initially, the position of the H atoms has been optimized without relaxing the metal frame. The two H atoms are bound to Cu_3 with slightly different Cu−H distances, 1.64 and 1.70 Å, Figure 2a. When the relaxation of the metal is allowed, however, there is a significant change in the Cu_3 structure, which becomes a nearly equilateral triangle with Cu−Cu distances of 2.50 and 2.42 Å, Figure 2b; the Cu−H distances, 1.64 and 1.74 Å, practically do not change from the previous optimization. The charge distribution in the fully optimized system shows an accumulation of electronic charge on the H atoms that assume hydride character, Table 1.

Cu_3 supported on a NBO center, NBO−Cu_3, has an almost equilateral triangular shape, Figure 3a, at variance with the gas-phase structure. This can be explained by the partial transfer of the unpaired electron from Cu_3 to the paramagnetic NBO center.[34] Notice that supported Cu_3 is bound through electrostatic forces also to a two-coordinated O site of the silica surface, Figure 3a. To study the products of the H_2 dissociation, two H atoms were placed in the corresponding position of free Cu_3, i.e., bridging the Cu−Cu bonds. The optimal metal−hydrogen distances obtained for a rigid NBO−Cu_3 substrate, $\sim 1.64 \pm 0.04$ Å, are slightly smaller than those found for the isolated cluster. When the Cu_3 unit is allowed to relax, the H_2 adsorption process induces a severe change in the position of the Cu atoms,

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TABLE 2: Energetics of H₂ Dissociative Adsorption on Free and Supported Cu₃ and Cu₅ Clusters and on Cu₃₄ Model of the Cu(111) Surface

system	optimized atoms	D_e/atom, eV[a]	ΔE, eV[b]	E_{relax} (Cu$_n$), eV[c]	E_{relax} (SiO₂), eV[d]
Cu₃₄(111) (T)	2H	2.13	+0.58		
Cu₃₄(111) (O)	2H	1.99	+0.87		
Cu₃ + 2H	2H	2.61	−0.37		
	Cu₃ + 2H	2.67	−0.50	0.13	
NBO−Cu₃ + 2H	2H	2.65	−0.46		
	Cu₃+2H	2.87	−0.90	0.44	
	SiO₂ + Cu₃ + 2H	2.89	−0.94		0.05
Cu₅ + 2H	2H	2.26	+0.32		
	Cu₅ + 2H	2.34	+0.17	0.15	
NBO−Cu₅ + 2H	2H	2.15	+0.54		
	Cu₅ + 2H	2.98	−1.13	1.67	
	SiO₂ + Cu₅ + 2H	3.03	−1.22		0.10

[a] Desorption (or dissociation) energy of a single H atom; a positive value corresponds to a bound state. *[b]* Energy balance for H₂ dissociative adsorption; a positive value of ΔE corresponds to an endothermic process. *[c]* Energy gain associated with Cu$_n$ relaxation. *[d]* Energy gain associated with SiO₂ relaxation.

which can be described as an opening of the triangle with formation of a bent structure, Figure 3b. One of three Cu−Cu distances increases from 2.43 to 3.28 Å, clearly indicating the breaking of a metal−metal bond. Notice that exactly the opposite occurs on the free cluster: by addition of hydrogen one of the Cu−Cu distances decreases, and the metal−metal bond is reinforced (this is the Cu−Cu bond that is not bridged by the H atom; see Figure 2a and 2b). The average Cu−Cu coordination number in the supported cluster decreases from 2 to 1.3 by adsorption of two H atoms. So far, we have only allowed the structure of the supported Cu₃ and of the two H atoms to vary but not the silica substrate. However, when this is done, there is no substantial change in the geometry of the complex. The charge distribution of the final structure is similar to that of gas-phase Cu₃, with the H atoms carrying a partial negative charge and Cu a positive one, Table 1.

We consider now the H₂ adsorption on free Cu₅. The structure of gas-phase Cu₅ is planar, Figure 4a, with Cu−Cu distances of 2.44 ± 0.04 Å; the average coordination number is 2.8. Initially, the two H atoms have been placed in the 3-fold hollow sites of the structure, the preferred adsorption sites on the (111) surface. The optimization process was first performed with fixed Cu positions and leads to a structure where the adsorbed H atoms are bridge bonded to Cu, Figure 4a. The Cu−H distances, 1.63 and 1.78 Å, respectively, are similar to those found for Cu₃, i.e., one long and one short. When a complete relaxation of the metal unit is allowed, the structure changes and results in a pentagonal ring of Cu atoms with two of the Cu−Cu bonds bridged by H atoms, Figure 4b. The structure is no longer planar. The average coordination number of the Cu atoms is then reduced from 2.8 to 2, and the Cu−Cu distances, ∼2.40 Å, are shortened with respect to the bare cluster. The shortening of the Cu−Cu distances induced by H adsorption is therefore a feature common to both Cu₃ and Cu₅. Also the Cu−H distances change and become more uniform, 1.65 and 1.69 Å, respectively, Figure 4b. The spin density is mainly located on Cu atoms not interacting directly with two H atoms, Table 1.

When deposited on a NBO center on the silica surface, Cu₅ keeps more or less the structure that it has in the gas phase (the main difference is a partial loss of planarity, Figure 5a). The adsorption of two H atoms placed on the 3-fold hollow sites, in the absence of any relaxation of the Cu cluster and of the SiO₂ substrate, results in a local minimum with an energy about 0.5 eV higher than the reactants, Table 2. When the Cu atoms are allowed to relax, a strong reorganization of the structure

occurs and the initial nearly planar structure, which can be seen as a section of the (111) surface, evolves in a capped square structure with some resemblance to the (100) pattern. The mean coordination number changes from 2.8 to 2.4. The optimization of the whole structure, including the silica support, induces no significant additional changes in the metal frame or in the Cu−H bonds.

3.2. Energetics of H₂ Dissociative Adsorption. In Table 2 we report the following quantities: (a) the desorption or dissociation energy of an H atom from the free or supported Cu cluster; (b) the energy balance for dissociative adsorption (i.e., the adsorption energy of two H atoms computed with respect to the cluster and to the H₂ molecule; here a negative energy corresponds to a bound state and hence to an exothermic process); (c) and (d) the energy gains associated with the relaxation of the Cu and SiO₂ units, respectively. The dissociation energy, D_e, of the H₂ molecule is 4.84 eV in our approach (the experimental D_0 value is 4.48 eV).[41]

The adsorption of atomic H is always an exothermic process (positive desorption energy); the computed values range from about 2 eV for the Cu(111) surface to almost 3 eV for supported Cu₅, Table 2. Since the energy required to break the H−H bond is about 5 eV, it is clear that some of the systems under investigation give rise to an exothermic H₂ dissociative adsorption, while others imply an endothermic reaction. In particular, when the H binding energy is smaller than ≈2.5 eV, the dissociative adsorption is thermodynamically unfavorable.

H atoms placed in tetrahedral, T, and octahedral, O, sites of the Cu₃₄ cluster model of the Cu(111) surface are in a local minimum but are not stable with respect to formation and desorption of molecular hydrogen. The dissociative adsorption is predicted to be endothermic by 0.58 eV on the T sites, and by 0.87 on the O sites. These values represent upper bounds because the geometry of the Cu₃₄ cluster was kept fixed; surface relaxation is going to stabilize the atomic adsorption state and to reduce the endothermicity of the reaction. Furthermore, if one takes into account the zero point energy of the H₂ molecule, about 0.3 eV,[41] the reaction is predicted to be only weakly endothermic. This is consistent with several theoretical and experimental results which show that on the Cu single crystal surfaces and at low H coverage the dissociative adsorption is an activated and thermoneutral process.[12] Heats of adsorption of about 0.5 eV have been measured only for H₂ dissociatively chemisorbed on stepped surfaces, on Cu powders, or on Cu particles deposited on SiO₂.[17] This suggests that a major role in the H₂ dissociation is played by the low-coordinated sites present on these systems.

On gas-phase Cu₃ dissociative adsorption is weakly exothermic, by 0.37 eV, for the frozen Cu₃ structure. The relaxation of the copper ring leads to an energy gain of 0.13 eV, and the final reaction is exothermic by 0.50 eV, Table 2. Experimentally H₂ dissociation on gas-phase, mass-selected Cu₃ clusters has not been observed.[18] This can be explained with a too high barrier for H₂ dissociation, which could make the reaction too slow to be observed in the time scale of the experiment. The same reaction on the silica-supported Cu₃ leads to a larger energy gain. For supported Cu₃ with frozen geometry the energy gain is 0.46 eV, a value that increases to 0.90 eV when Cu relaxation is allowed, Table 2. The relaxation of the substrate, on the other hand, contributes only 0.04 eV to the stability of the complex, Table 2. Overall, H₂ dissociation on supported Cu₃ is about 0.4 eV more exothermic than in the gas phase.

On gas-phase Cu₅ the dissociative adsorption of H₂ is an endothermic process; on the frozen structure the ΔE is of +0.32

eV, a value that decreases to +0.17 eV after cluster relaxation, more or less the stabilization found for Cu_3. This result is consistent with the experimental observation that gas-phase Cu_5 and, in general, small mass-selected Cu clusters do not react with H_2.[18] When the supported Cu_5 complex is considered, the dissociative adsorption on a fixed Cu_5 structure is even more endothermic than that on the gas-phase cluster, $\Delta E = +0.54$ eV, Table 2. However, when the Cu atoms are free to relax and to undergo the strong geometrical change described in the previous paragraph, the final product becomes strongly stabilized and the process is exothermic by 1.13 eV, Table 2. The additional relaxation of the SiO_2 substrate contributes only 0.09 eV to the total stability. *Thus, while gas-phase Cu_5 does not promote the dissociative adsorption of H_2, the same cluster deposited on a silica support becomes an active catalyst for the process!* The role of the adsorbed H atoms in stabilizing the new structure, Figure 5b, is demonstrated by the fact that without the two H atoms the $NBO-Cu_5$ structure reported in Figure 5b is 0.9 eV less stable than the optimal structure, Figure 5a.

Several effects can in principle contribute to the higher reactivity of the supported clusters. One is a different position of the 3d levels, but we have no clear evidence that this is important, nor is the change associated with the 3d orbital population significantly different in free and supported clusters. The reduced electron density on supported Cu clusters, which donates charge to the NBO,[34] acts to reduce the Pauli repulsion with the adsorbate and could in principle favor an initial charge transfer from the σ bonding orbital of the hydrogen molecule to the metal, as has been suggested by Muller.[15] The formation of a closed-shell species, and the over-coordination of two Cu atoms of the cluster to oxygen atoms of the silica surface can also be responsible for the higher stability of the products. Probably all these effects cannot be decoupled, but no matter which is the most important contribution, there is a clear electronic role played by the substrate.

4. Conclusions

In this study we have considered the reaction of the H_2 molecule with free and supported Cu clusters. As a support we considered the SiO_2 substrate, which is widely used in catalysis to disperse metal particles. On the basis of previous studies that have shown the importance of point defects on the SiO_2 surface to favor the nucleation of the metal particle and to block its diffusion on the silica surface,[26,33,34] we have considered Cu_3 and Cu_5 clusters anchored to a nonbridging oxygen center, a paramagnetic defect present on the surface of dehydroxylated silica.[29] For comparison, we also considered the same process on a well-defined crystallographic face of metallic Cu; to this end we used a Cu_{34} model of the Cu(111) surface.

On the free, gas-phase, metal clusters hydrogen dissociative adsorption is weakly exothermic (Cu_3) or moderately endothermic (Cu_5); in both cases the reactivity of the cluster is low. This is in broad agreement with the experimental observation that mass-selected Cu clusters containing 1−14 metal atoms do not react with H_2.[18] Of course, kinetic aspects connected to the fact that H_2 dissociation is an activated process also play a role. In a similar way, the regular Cu(111) surface exhibits low reactivity. On our Cu_{34} model the H_2 dissociation is an activated process and the reaction is endothermic. Also in this case the result is in general agreement with the finding that single-crystal Cu surfaces are unreactive,[16] at variance with Cu powders, films, or silica-supported Cu particles for which heats of adsorption of about 0.5 ± 0.1 eV have been measured.[17] This different

behavior may be connected to the presence of low coordinated sites. Several explanations have been invoked to explain the low reactivity of Cu. Most of them are connected to the fact that the Cu 3d band is full and is situated below the Fermi level.[16]

When the same Cu clusters, which in the gas-phase are rather inert, are deposited on the NBO site of the SiO_2 substrate, we found an enhanced reactivity that increases the exothermic character of the dissociative adsorption for Cu_3 and which even reverses the sign of the energy balance for Cu_5: while in the gas phase the process is endothermic, it becomes highly exothermic on supported Cu_5. This different reactivity is accompanied by a strong structural change of the supported metal clusters upon H_2 chemisorption, which leads to completely different hydrogenated complexes than found in the gas phase. Thus, the interaction with the SiO_2 support turns rather inactive Cu clusters into active catalysts for H_2 dissociation.

An important question that follows from this finding is the following: "is the change in reactivity dominated by geometric or by electronic effects"? While it is true that a regular SiO_2 surface does interact only weakly with supported metals, point defects interact more strongly and perturb the cluster electronic structure in a more pronounced way. The interaction with a NBO center leads to a decrease of the electron density on Cu, an effect that seems to stabilize the adsorbed H atoms. This can be connected to a reduced Pauli repulsion in the initial stage of the interaction. Probably more important from the electronic point of view is the partial rehybridization of the d and of the sp orbitals upon deposition of the cluster on the substrate. Finally, also the electrostatic interactions of some of the Cu atoms of the cluster (which donate electronic charge to the H atoms) with the bridging oxygens of the SiO_2 surface contribute to stabilize the unusual structures of supported Cu clusters with adsorbed H. This seems to indicate that geometrical and electronic effects are strongly mixed in, making a clear-cut separation of their importance difficult, if not impossible.

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