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III INTERNATIONAL CONFERENCE "CATALYSIS: FUNDAMENTALS AND APPLICATIONS"

Stereoselective Hydrogenation of Acetylene on Copper Catalysts: A Quantum-Chemical Study

M. Zh. Zhaksibaev[a], **S. E. Malykhin**[b], **Yu. V. Larichev**[b], **and A. M. Pak**[a]
[a] *Institute of Organic Catalysis and Electrochemistry, Academy of Sciences of Kazakhstan, Almaty, Kazakhstan*
[b] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
e-mail: malykhin@catalysis.ru

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Abstract—The structure of the alkyne adsorption complex on the copper surface is favorable for the stereoselective formation of *cis* isomers in the hydrogenation reaction. The pathway of dissociative hydrogen adsorption on copper is reported. It is assumed that the electron-donating promoter acts to reduce the electron work function of the copper catalyst by partially covering or "decorating" the surface of the copper particles.

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INTRODUCTION

Alkyne hydrogenation is used both in the industrial removal of acetylene from ethylene and in small-scale processes of selective (stereoselective) hydrogenation [1, 2]. Various types of catalysts are used in these processes [3, 4]. Most of them are modifications of the partially poisoned Pd catalyst [2], Pd–Cu bimetallic catalysts [4–6], or copper catalysts (oxide-supported Cu particles). The Cu/γ-Al_2O_3 catalysts are considerably cheaper than the common Pd systems [4, 7–9] and have similar productivity characteristics. The Cu systems are promoted by electron-donating admixtures [8–12], mainly compounds of rare-earth elements, to improve their catalytic properties.

Hydrogen dissociation on copper is forbidden by the principle of molecular orbital symmetry [13]. The *d* orbital of the copper atom is filled, and the highest occupied molecular orbital (HOMO) is the symmetric Cu 4*s* orbital. During the reaction, this orbital is transformed into an antisymmetric σ-antibonding H–H orbital. The increase in the electron kinetic energy associated with this transformation results in a high activation barrier to the reaction. The activation barrier can be lowered by photochemical excitation or by electron density transfer to metallic copper, a process producing a similar effect.

Based on these facts, we can assume that the role of the electron-donating promoter is to transfer electron density to copper and to facilitate the dissociative adsorption of hydrogen. However, as in many similar cases [14–16], the promoter does not change its oxidation state.

Thus, the effect of the promoter and the mechanism of the overall triple bond hydrogenation reaction on the copper catalyst are not understood completely. The purpose of this work is to study the reaction mechanism and to discuss the role of the promoter.

EXPERIMENTAL

According to our study [17], the general structure of hydrogen adsorbed on Cu_n clusters (n = 1–14) is a planar pentagon formed by three copper atoms and two hydrogen atoms (Fig. 1). This cluster was chosen for quantum-chemical simulation of the dissociative adsorption of hydrogen. The five-atom copper cluster was examined in the conformation corresponding to a local minimum rather than the global minimum (Fig. 1). This was done for two reasons. Firstly, we wished to save computational time. Secondly, the cluster conformation at the global minimum point is planar, and this cluster will radically rearrange its structure upon the adsorption of acetylene, ethylene, or hydrogen. This is poorly consistent with the real behavior of a large copper particle. The densely packed local conformation of Cu_5 relaxes to a lesser extent, in accordance with what is expected of a large particle.

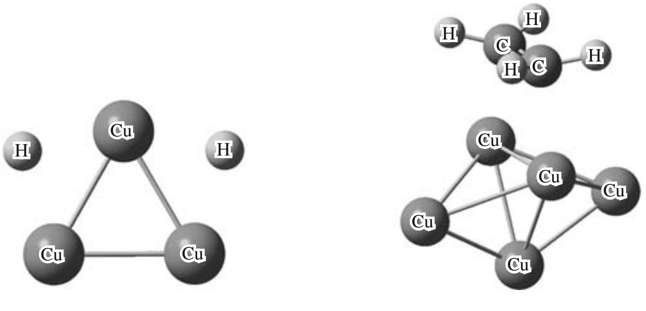

Fig. 1. Model copper clusters.

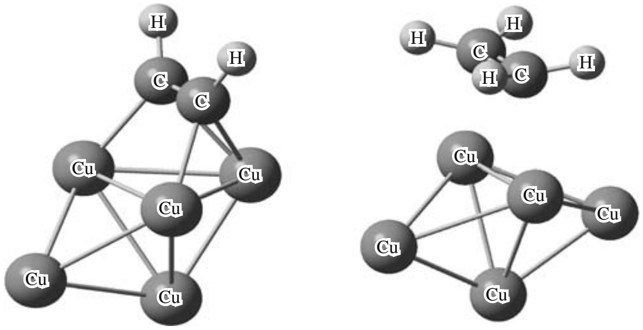

Fig. 2. Adsorption complexes of acetylene and ethylene on the copper cluster surface.

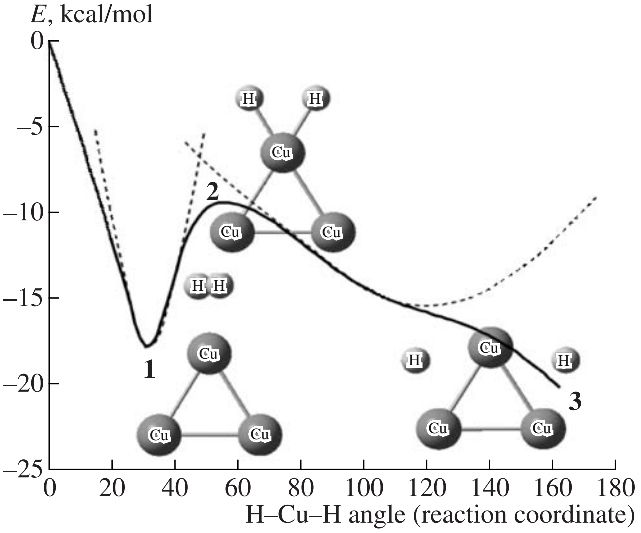

Fig. 3. Energy profile of the dissociative adsorption of hydrogen on the copper cluster.

The effect of the promoter and support on the electronic structure of the copper active site was simulated by varying the charge of the Cu_3 copper cluster from +1 (copper on the electron-withdrawing support Al_2O_3) to –1 (promoter effect).

All calculations were performed using density functional theory (DFT B3LYP method) and the Gaussian 03 program package. The basis sets were LANL2DZ, 6-31G(d), and 6-31+G(d) for the clusters Cu_5, Cu_3, and Cu_3^-, respectively. The pathway of the dissociative adsorption of hydrogen was calculated by variation of the H–Cu–H angle with optimization of the other degrees of freedom.

RESULTS AND DISCUSSION

According to our calculated data, acetylene forms a stable adsorption complex with a bond energy of 26 kcal/mol on the copper surface. Due to adsorption, the carbon atoms acquire an sp^3-hybrid structure in which the C–H bonds are directed away from the copper surface (Fig. 2). Evidently, substituents that are bulkier than hydrogen atoms would also point away from the surface. No step of the hydrogenation reaction changes the orientation of the bulky substituents with respect to the surface. Thus, the structure of the adsorption complex of alkyne with copper is favorable for the highly selective formation of *cis* isomers.

The earlier estimates of the activation energy of dissociative hydrogen chemisorption lie in the range from 10 to 34 kcal/mol [13, 17] (the mean is ~14 kcal/mol). The desorption energy of the hydrogenation product (ethylene) is of the same order (14 kcal/mol [13, 17]). Since the reaction rate is determined by hydrogen dissociation [17], the entropy change should be taken into account along with the enthalpy factor. Ethylene desorption increases the entropy of the system because it yields a gas. At the same time, hydrogen adsorption is an entropically unfavorable process. However, the decrease in entropy is considerably lower in the case of the formation of a two-dimensional gas of hydrogen atoms that do not leave the catalyst surface (the motion component orthogonal to the catalyst surface is absent) but move freely on the surface. This phenomenon is known as spillover. The occurrence of spillover in the promoted Cu/γ-Al_2O_3 system is indirectly confirmed by the fact that the amount of hydrogen on the promoted catalyst exceeds the amount of hydrogen on the initial, unpromoted catalyst by a factor of 2.4 [18].

According to the calculated data, the vibrational frequencies of the $(Cu_3H_2)^-$ cluster (“promoted system”) are lower than those of the uncharged cluster Cu_3H_2. The appearance of the thermodynamically occupied low frequencies ($h\nu < kT$), which are responsible for “pseudotranslations” of hydrogen atoms on the copper surface, indicates an enhanced mobility of the hydrogen atoms.

It is essential that adsorption species **1** (Fig. 3) is unstable on the negatively charged cluster. For the neutral cluster, this adsorption species occurs at a local minimum (species **3** is lower than species **1** by 28 kcal/mol). For the positively charged cluster, the energy difference between species **3** and **1** is less than 5 kcal/mol (table).

The energy profile of the dissociation reaction of molecular hydrogen on the copper cluster is shown in Fig. 3. Despite its obvious exothermicity, the reaction has an activation barrier, which, as was shown for the Cu_n clusters with $n = 4–9$ [17], does not correlate with the heat of the reaction. This fact is formally in conflict with the Brønsted–Evans–Polanyi rule [19, 20], according to which the heat of a reaction and its activation barrier are linearly related. The Brønsted–Evans–Polanyi rule is widely used in catalysis; however, it is inapplicable to this reaction and, therefore, cannot provide a correct prediction. As can be seen from Fig. 3, the energy profile cannot be described in terms of two parabolas: species **3** (product) is far away from transi-

Heats of formation (kcal/mol) of differently charged copper–hydrogen clusters (see Fig. 3)

Cluster	**1**	**2**	**3**
$Cu_3H_2^-$	Does not exist	Does not exist	–24
Cu_3H_2	–15	–10	–43
$Cu_3H_2^+$	–13	+47	–18

Note: The heats of formation were calculated as $E = E(Cu_3^{n=+1,0,-1}H_2) - E(Cu_3^{n=+1,0,-1}) - E(H_2)$.

tion state **2**, and the descent from **2** to **3** is rather flat. The Brønsted–Evans–Polanyi rule is based on Hammond's postulate: if two states occur consecutively and have approximately equal energies, their interconversion will induce only a small reorganization of the molecular structure. Hydrogen dissociation on copper is a reaction with a "non-Hammond" energy profile, and, therefore, its activation energy is not correlated with its heat.

Our calculations indicate that the state of copper favorable for catalysis is $Cu^{\delta-}$. However, oxide supported copper is known to exist as Cu crystallites and Cu^+ and Cu^{2+} ions stabilized on the support. The hypothetical state Cu^- was not observed in copper catalysts [11, 12, 21–26]. If this state existed, it would be detectable by XPS and IR spectroscopy (IR spectroscopy of adsorbed probe molecules). Below, we will attempt to resolve the contradiction between theory, according to which the presence of Cu^- is necessary, and the actual absence of this state in active systems.

The high barrier to the dissociative adsorption of hydrogen is due to the breaking of the symmetry of the electron wave function. Theoretically, the reaction can proceed as photochemical. Photon absorption results in a reversal of the dipole moment of the reacting system. This causes electron density redistribution favorable for the reaction. Indeed, the direction of the dipole moment of transition state **2** is opposite to that of reactant **1** (Fig. 4).

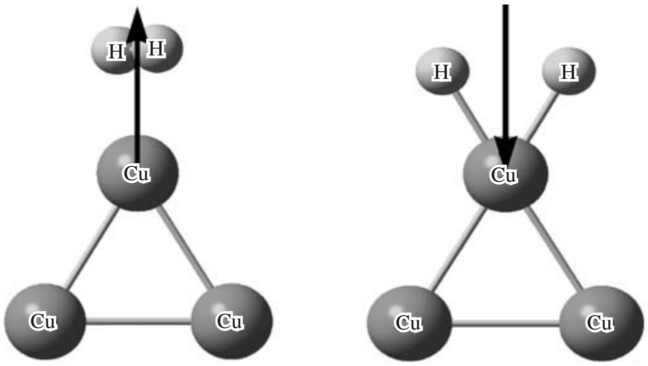

Fig. 4. Dipole moment vectors of the initial hydrogen-on-copper cluster and of the activated complex.

The change of the dipole moment of reactant **1** toward values characteristic of **2** would lower the activation barrier. A change in the dipole moment is a lower order effect than a change in the atomic charge, yet it is quite significant. A change in the local dipole moment implies a change in the electron work function of the catalyst surface, a global (integral) characteristic of the system. There is good reason to assume that the promoter serves to decrease the electron work function of the copper catalyst. This hypothesis eliminates the above contradictions and agrees well with experimental data [14–16, 18, 27].

Earlier, it was found that the addition of a promoter decreases the active surface area of the catalyst. For instance, promoting the copper catalyst with 1–10% Eu reduces its surface area from 68 to 48 m^2/g [18]; however, the catalytic activity increases and peaks at a Eu content of 5%. Eu_2O_3 partially covers the copper catalyst surface, shifts the electron cloud of metallic copper, and thus facilitates electron withdrawal from the metal or, at the local atomic and molecular level, changes the dipole moment of the hydrogen–copper system. Further raising the promoter content simply blocks the surface accessible to the adsorbate, thus reducing the catalytic activity. A similar decrease in the electron work function is observed for other systems. For example, alkali metal cations on ruthenium particles reduce the electron work function of ruthenium and this effect favors dinitrogen dissociation, the rate-determining step of ammonia synthesis [27].

CONCLUSIONS

According to our calculations, the adsorption complex of the alkyne with the surface of the $Cu/\gamma\text{-}Al_2O_3$ catalyst is favorable for stereoselective hydrogenation into the *cis* isomer. The substituents in the adsorbed alkyne point away from the copper surface, and, since the reaction takes place in the surface plane, it does not change their spatial orientation.

The pathway of the dissociative adsorption of hydrogen on copper was studied. The activation energy of this process does not correlate with the heat of the reaction, because the energy profile is "non-Hammond": it cannot be described in terms of two parabolas, because the product is far from the transition state along the reaction coordinate.

It was assumed that the role of the electron-donating promoter is to decrease the electron work function of the copper catalyst by partial coating or "decoration" of the copper particle surface. The change in the electron work function, which is an integral (global) characteristic of the system, is due to the change in the local dipole moment of the copper–hydrogen molecule system accompanying the electron density redistribution favorable for hydrogen dissociation.

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