



DFT simulations and microkinetic modelling of 1-pentyne hydrogenation on Cu₂₀ model catalysts



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ABSTRACT

Adsorption and dissociation of H₂ and hydrogenation of 1-pentyne on neutral and anionic Cu₂₀ clusters have been investigated using the density functional theory and microkinetic modelling. Molecular adsorption of H₂ is found to occur strictly at atop sites. The H₂ dimer is activated upon adsorption, and the dissociation occurs with moderate energy barriers. The dissociated H atoms reside preferentially on 3-fold face and 2-fold edge sites. Based on these results, the reaction paths leading to the partial and total hydrogenation of 1-pentyne have been studied step-by-step. The results suggest that copper clusters can display selective activity on the hydrogenation of alkyne and alkene molecules. The hydrogenated products are more stable than the corresponding initial reactants following an energetic staircase with the number of added H atoms. Stable semi-hydrogenated intermediates are formed before the partial (1-pentene) and total (pentane) hydrogenation stages of 1-pentyne. The microkinetic model analysis shows that C₅H₁₀ is the dominant product. Increasing the reactants (C₅H₈/H₂) ratio enhances the formation of products (C₅H₁₀ and C₅H₁₂).

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1. Introduction

Heterogeneous catalytic hydrogenation is one of the most important chemical reactions in the modern chemical industry. Selective hydrogenation of alkynes and alkenes remains still an important topical issue in modern heterogeneous catalysis, which is an industrially significant reaction and has particular relevance in the petrochemical industry [1]. Much of the work in this area has concentrated on low molecular weight species such as ethylene and acetylene [2]. However, more recently research interest has focused on the hydrogenation of higher molecular weight molecules [3]. The initial dissociation of the hydrogen molecule is known to be a vital step in these processes, and extensive efforts have been devoted to understand the dissociative adsorption of H₂ [4–7]. Catalysts made of platinum, palladium, or other expensive (precious) metals are often required to promote H₂ dissociation [3–7]. Particularly, palladium is known to be one of the most selective catalysts for the hydrogenation of highly unsaturated hydrocar-

bons [8,9]. The limited natural resources pose severe challenges for the availability of the platinum group metals (PGMs), and it is highly desirable to achieve similar catalytic performance with the optimum particle size and composition (materials efficiency) or less rare metals, even completely without them by using earth-abundant alternatives (replacement).

Copper based catalysts have shown good activities for a variety of reactions [10–12] and they have been widely used in many heterogeneous catalytic processes. Moreover, Cu nanoparticles are among the most important catalysts for hydrogenation in many heterogeneous catalytic reactions [13]. Previous theoretical work on hydrogen interaction with copper falls into two general categories. The first consists of studies of small clusters up to 15 atoms [14,15]. The second involves investigations of Cu surface models with the aim of interpreting experimental results on various crystalline surfaces [16,17]. Calculations of the crystalline surface models have provided rich information on the detailed processes of surface reactions. However, studies have shown that for the same chemical process, the thermochemical energies as well as the activation barriers can differ on different crystalline facets [18]. This suggests that the detailed atomic arrangements of the catalysts has a profound influence on the catalytic activities. Since the size-dependent atomic packing of clusters can differ significantly

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from each other and from the bulk, their reactivity with molecular species is also expected to exhibit a rich variety. This is similar to what was found for crystalline surfaces, where sharp corners, vacancies and highly exposed metal atoms are often more reactive than the atoms embedded in a flat surface [18]. Understanding the mechanisms that govern the interaction between the molecular species to be catalyzed and the catalyst clusters is a topic of active research.

Computational modelling is important for the catalysis research and development [19,20]. Within this context, a structural and energetic characterization of the catalytic sites as well as the molecular level studies on the interactions between adsorbate and adsorbent are of primary importance. The basic idea for the catalyst simulations is that chemisorption and reactivity are local phenomena, which are primarily affected by the surface structure nearest the active sites, and one can use finite atomic models to describe the components involved in the reaction and the region surrounding the active site. Here, we shall focus on modelling catalyst nanoparticles in the framework of metal clusters which may have special properties due to clusters' size-dependent morphological and electronic characteristics.

In this article, we report a computational study performed on a model catalyst Cu_{20} cluster for the hydrogen dissociation and hydrogenation of 1-pentyne using a combination of density functional theory (DFT) and microkinetic modelling. The reason to choose 1-pentyne as the target molecule is that there is significantly less information in the literature about gas-phase hydrogenation involving longer-chain alkynes, especially in terms of theoretical aspects. To hydrogenate 1-pentyne, atomic hydrogen should be available, which can be obtained from the dissociative reaction of molecular hydrogen. In our study, the reaction mechanisms were simulated using neutral (Cu_{20}) and anionic (Cu_{20}^-) clusters, which include the effects of changing charge state and electronic shell closing/opening. The addition of one electron makes the two clusters distinct from each other which affects the cluster geometry also. In the following, the interaction mechanisms, energy barriers, intermediate species and kinetics involved in the reactions on the catalyst nanoparticles are reported.

2. Computational methods

To ensure physically meaningful results for calculated cluster properties, the correct atomic arrangements for the corresponding clusters must be used in the calculations. The structures used for the Cu_{20} and Cu_{20}^- clusters are the lowest-energy isomers obtained in an extensive, unbiased search for the ground state cluster geometries over the size range $n = 2-30$ [21,22]. The geometry of Cu_{20} can be viewed as a capped icosahedral (I_h) structure in which seven capping atoms bond with each other and cover the 13-atom I_h core. A capped 19-atom double icosahedral (D_{5h}) structure is identified as the most stable geometry for Cu_{20}^- .

2.1. DFT simulations

The DFT simulations were carried out using the spin-polarized, gradient-corrected functional of Perdew, Burke, and Ernzerhof (PBE) [23] as implemented in the CP2K package [24,25]. In addition to PBE, the hybrid PBE0 [26,27] and B3LYP [28,29] functionals were used to cross-check the energy ordering of activation energy barriers for monitoring the effect of different exchange-correlation functionals. The wave functions were expanded in a molecularly-optimized double-zeta valence plus polarization (DZVP) Gaussian basis set [30], which has been optimized to reduce the basis set superposition error (BSSE) in CP2K. An additional auxiliary plane wave basis of 400 Ry energy cutoff was used for the calculation

of the electrostatic energy terms in the DFT total energy functional. The valence electron-ion interaction is based on the norm-conserving and separable pseudopotentials of the analytical form derived by Goedecker, Teter, and Hutter (GTH) [31]. The periodic boundary conditions were switched off by using a Wavelet-type Poisson solver in a cubic simulation box of 15 Å sides for Cu_{20} and 20 Å sides for Cu_{20}^- clusters. Spatial charge decomposition among atoms was analyzed using the Bader algorithm [32]. The dissociation and reaction pathways were mapped using the Nudged Elastic Band method with the Climbing Image algorithm (CI-NEB) [33]. The nature of each structure, both the minima and the transition states, was identified by vibrational analysis, from which zero-point energy (ZPE) corrections were obtained and included in all adsorption energies, activation energy barriers, and reaction energies calculations. No symmetry constraints were imposed in structural relaxations.

2.2. Microkinetic modelling

Microkinetic modelling is a powerful computational analysis tool, which is used to examine catalytic reaction systems in terms of elementary reactions and their interactions without making any a priori assumption for the rate-determining steps in the reactions or surface coverages of intermediates. In this way, reaction modelling can incorporate the measured or calculated/estimated physical and chemical parameters in the rate expressions

In order to study the surface reactions, the kinetic rates were quantified. The forward rate constant ($k_{f,i}$) of each reaction was calculated using the Eyring equation [34] in the harmonic approximation based on transition-state theory:

$$k_{f,i} = \frac{k_B T}{h} e^{-\frac{\Delta G_i^\ddagger}{k_B T}} \quad (1)$$

where k_B is the Boltzmann's constant, h is the Planck's constant, T is the absolute temperature, and ΔG_i^\ddagger is the Gibbs activation free energy for the reaction pathway i (see supplementary information). The reverse rate constant ($k_{r,i}$) was calculated similarly and the thermodynamic equilibrium constant K_i was calculated from the Gibbs free energy of reaction ΔG_i^\ddagger (see supplementary information).

$$K_i = \frac{k_{f,i}}{k_{r,i}} = e^{-\frac{\Delta G_i^\ddagger}{k_B T}} \quad (2)$$

For the unimolecular adsorption process the forward rate was approximated using the particle flux from the kinetic gas theory [34]:

$$k_{f,i} = \frac{P\sigma(T, \theta)}{\sqrt{2\pi m k_B T}} A_i \quad (3)$$

where the P is the partial pressure of the adsorbant, m is mass of the precursor molecule and A_i is the area of the adsorption site i . In our calculations the area of adsorption site was approximated as the reciprocal of the surface adsorption density. $\sigma(T, \theta)$ is the sticking probability of the adsorbant, which was assumed not to be directly affected by temperature and was approximated by the fractional coverage of the free adsorption sites (see supplementary information). To reinforce thermodynamic consistency, the reverse rate constant was computed using

$$k_{r,i} = \frac{k_{f,i}}{K_i} \quad (4)$$

With the forward and reverse rate constants defined, we solved the full set of steady-state rate equations to obtain the surface coverages of all possible reaction intermediates and the fraction of free

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