Aerobic oxidation of alkanes on icosahedron gold nanoparticle Au55

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A B S T R A C T

Aerobic oxidation of cyclohexane, propane, ethane, and methane to the corresponding alcohols was investigated over an Au55 gold nanoparticle with icosahedron symmetry using density functional theory. Reaction mechanisms were elucidated and activation barriers for catalytic C—H bond cleavage and corresponding alcohols' formation were estimated. Furthermore, on the basis of the reaction rate constants calculated for realistic reaction temperatures, the relative reaction rates for each alkane hydroxylation were discussed. The catalyst selectivity was investigated for the formation of primary and secondary alcohols. All reaction mechanisms for alkane hydroxylation are compared with the catalytic dissociation of dioxygen molecule over gold nanoparticle surface, which is an important precursor reaction for aerobic oxidation. We have further investigated overoxidation reaction mechanisms leading to formation of ketones. Our results are compared with experimental findings to provide important guidelines for the tuning of catalytic reactions towards the desired products and reaction conditions.

1. Introduction

Hydroxylation of alkanes is a key industrial process which is an initial step of the conversion of hydrocarbons to more valuable chemicals used in the preparative and synthetic chemistry [1]. Large variety of catalysts were employed in the process ranging from homogeneous catalysts to various heterogeneous materials [2], and bio- and enzymatic catalysts [3]. Direct alkane hydroxylation is a difficult reaction because it proceeds through a C—H bond cleavage, which usually requires significant activation energy. The C—H bond is characterized with dissociation energy of 104 kcal/mol for methane, 98 kcal/mol for ethane, 95 kcal/mol for the secondary carbon atom of propane, and 100 kcal/mol for cyclohexane [4]. Owing to the close electronegativity of carbon and hydrogen, the C—H bond is covalent and non-polar, which makes it difficult to destabilize or cleave by means of electrostatic interactions or charge transfer processes. Amongst the alkane C—H bonds, the highest energy is required for the cleavage of the bonds of methane, due to the formation of highly reactive methyl radical species. The direct hydroxylation reaction of methane is considered to be a dream process in the small, energy molecules chemistry [5]. Methane is the main component of natural gas and a high-energy molecule, which combusts completely forming carbon dioxide and water. The process is used in thermal electrical power plants and internal combustion engines. Electrochemical oxidation of methane without combustion is performed in solid oxide fuel cells [6]. Significant drawback of methane as a fuel is its transportation because it has high molar volume and low compressibility factor. Thus, transportation of methane requires high pressure vessels and pipelines and significant energy is consumed for the gas compression. While methanol maintains the high energy of methane and can be used in combustion processes and fuel cell's electrochemical reactions, it is in liquid state at normal conditions, which makes it easy for transportation and storage.

Direct alkane hydroxylation is catalyzed by various transition metals as a part of organometallic compounds (homogeneous catalysis) or deposited on surfaces and three-dimensional porous materials (heterogeneous catalysis) [7,8]. In addition, in biological systems, metal centers catalyze C—H bond cleavage as a part of enzymatic active sites [9–12]. In a series of theoretical studies, the C—H bond dissociation was investigated on various transition metals and transition-metal oxides showing relatively low activation barriers for Ni, Cu, Fe, and Co [13–15]. Copper and dinuclear copper complexes immobilized in zeolites and as active sites of enzymes have proved to be good catalysts for aerobic C—H bond cleavage and consequent hydroxylation [16]. Depending on their cage size, some Cu substituted zeolite materials have shown remarkable selectivity towards methane and ethane oxidation to methanol and ethanol, respectively [17,18].

In homogeneous organometallic catalysis, the C—H activation can proceed through one of the following three mechanisms: oxidative addition, electrophilic activation, and σ-bond metathesis [19]. In the oxidative addition, a metal center is inserted between the carbon and the hydrogen atoms. As a result, the C—H bond is cleaved, and the metal is oxidized. The electrophilic activation is similar to the oxidative addition but is passing through oxidative transition state. In the σ-bond metathesis, the target hydrocarbon bond breaks as the carbon bonds to the metal and the hydrogen bonds to one of the metal's ligands. The reaction proceeds with different mechanism on metal surfaces where the metal hydrogen interaction is in general too weak to cleave the C—H bond under mild conditions [20]. However, in the presence of oxidative species the metal surface can play a role of a catalyst and can lower the activation barrier for the C—H dissociation [21,22]. One of the most often used catalytic materials for C—H bond cleavage and sequential oxidation is palladium [22–24]. Its surface is characterized with high catalytic activity; however, a significant drawback is that it shows low selectivity and often leads to complete oxidation of the alkanes, in particular methane, to carbon dioxide and water. The conversion of methane to methanol was achieved on Pd/Au nanoparticles under mild conditions [25]. Silver surfaces have also shown catalytic activity towards electrochemical and photochemical oxidation of alkanes [26].

Most often, hydrogen peroxide and dioxygen molecules are preferred oxidants for alkane oxidation. Hydrogen peroxide is a green chemistry oxidant with the only byproduct water. However, its production remains relatively expensive with main synthetic road utilizing the anthraquinone method, beside the recent advancements in the direct synthesis over Pd/Au nanoparticles [27,28]. Dioxygen is the preferred oxidant owing to its abundance; however, it can oxidize the metal catalyst's surface and, thus, can be used only with a limited number of materials.

The discovery of gold nanoparticle catalysis by Haruta [29] triggered widespread research on gold application to various chemical reactions such as CO oxidation [30–33], selective oxidation of hydrocarbons [34–37], selective hydrogenation of hydrocarbons [38], etc. Tsukuda and coworkers have demonstrated that ∼1 nm gold nanoparticles can be used for aerobic oxidation of various organic molecules [34–37]. While macroscopic gold is believed to be inert, gold nanoparticles with size below 5 nm show remarkable catalytic activity in processes where other materials often fail. Gold could adsorb the reactant molecules with the proper strength to activate them and could easily release the products [39]. Its mild activity allows for the selective catalysis of chemical reactions with limited window of activation energies, compared to more active catalysts such as platinum and palladium, which lead to catalysis with low selectivity over a vast range of reactions [40]. One of the reasons behind the remarkable properties of gold is considered to be the relativistic effects on its core electrons in comparison with other noble metals.

Gold nanoparticles show properties which differ from those of macroscopic gold. Beside the catalytic activity, gold nanoparticles possess different electronic and physical properties. Particles with size below 5 nm have size dependent melting temperatures because their geometric structures are characterized with several close-lying local minima [41,42]. The geometry of small size gold clusters depends on the supporting surface and the coordinating ligands. Other difference between macroscopic gold and gold nanoparticles is within their electronic spectra. Gold clusters under 150 atoms were shown to have band gap and semiconductor properties while larger particles and bulk gold show metallic properties. The band gap in less than 150 atoms gold clusters is strongly influenced by the cluster geometry and could affect the catalytic activity [40].

Recently, theoretical investigations revealed that methane can be adsorbed on a few hundred atoms gold nanoparticles [43]. The adsorption energy could be further fine-tuned by selecting the oxide support. It was shown that electron withdrawing supports increase the methane adsorption energy while electron rich supports reduce it. In a series of papers Tsukuda and co-authors have demonstrated that different hydrocarbons can be aerobically oxidized on gold clusters with size within 18–80 atoms [34,35]. Those reactions were particle size dependent with peak for particles of approximately 45–50 gold atoms, which corresponds to ∼1 nm diameter. It was reported that the catalyst is non-scalable, and the catalytic activity is lost for particles with more than 2 nm in diameter [36]. Tsukuda and co-authors have demonstrated that the reactions are independent from the support surface by demonstrating that they could proceed both on single-wall carbon nanotubes and hydroxyapatite [34,35]. However, the detailed mechanism of the alkane hydroxylation remains unclear, as well as, the possible selectivity of gold nanoparticle catalyst. In this study, we investigate the hydroxylation of cyclohexane, propane, ethane, and methane using density functional theory calculations. The investigated compounds allow us to compare the hydroxylation of n-alkanes versus cycloalkanes and the selectivity of the catalyst towards primary and secondary hydrogen atoms.

2. Methods of calculation

The calculations were performed using Turbomole 7.1 package for first-principle calculations [44,45]. We employed density functional theory (DFT) using the Perdew–Burke–Ernzerhof exchange-correlation functional (PBE) [46]. The PBE functional was selected as it describes well the properties of metals and can encounter well for the catalytic activity of gold. Geometry optimization, transition-state search, and frequency calculations were performed using double ζ, polarized, def2-SV(P) basis set of the Aldrich group while single-point energy calculations were performed using the larger, triple ζ, polarized, def2-TZVP, basis set. Core electrons of gold were described using def2-ECP (effective core potentials) which correctly describe the relativistic effect of core electrons [47]. All calculations were performed using spin-polarized wavefunction and dispersion interactions were included using Grimme DFT-D3 correction [48]. The initial geometry of the chemisorbed gas molecules was estimated using 300 fs (0.5 fs step) computational annealing technique (first-principle molecular dynamics) with starting temperature of 573 K and end temperature of 50 K. Estimating correctly the transition state is crucial for understanding the catalytic reactions. We have performed path optimization using 20 images with Linear Synchronous Transit/Quadratic Synchronous Transit (LST/QST) method. The path optimization was converged to forces under 0.05 eV/Å^2. The obtained geometry with maximum energy along the LST/QST path was used for local transition state search using Newtonian methods until geometry configuration was characterized by a single imaginary frequency along the reaction path. We have analyzed the reaction rates using the Arrhenius equation. For the similar reactions of alkane hydroxylation, we have assumed that the preexponential factor is the same and we have ignored its contribution to the reaction rate constant. We should note that this is a strong approximation and it is applied only to the same class of molecules and same reaction, i.e., hydroxylation of alkanes. Spin density maps were used to analyze the radical reaction mechanisms. Atomic and molecular charges were estimated using Mulliken populational analysis. It is worth noting that Mulliken analysis is dependent on the basis set. In our study Mulliken analysis was performed for the def2-TZVP basis set, single point calculations.