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Theoretical study of acetate decomposition on Au(111) surface: Oxygen-assisted γ -CH activation mechanism

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ABSTRACT

Inspired by the recent experimental results that the oxygen atoms adsorbed on Au(111) surface have a great influence on the mechanism and path of the decomposition of acetate (ACS Catal, 2014, 4(9): 3281–3288), the density functional theory was performed to simulate the decomposition of acetate on Au(111) surface with and without oxygen atom. The present calculation results show that the pre-adsorbed oxygen atoms on Au(111) surface can activate the γ -CH bond of acetate and reduce the activation energy of the reaction, then finally get the product of carbon dioxide and formaldehyde. While without adsorbed oxygen atoms, acetate on Au(111) surface breaks down into carbon dioxide and methyl through C-C bond cleavage. In addition, the decomposition of acetate on Ag(111) surface with pre-adsorbed oxygen atoms has also been simulated and that of Au(111), and it was found that the oxygen atoms on Ag(111) assist γ -CH bond activation more efficiently due to its more negatively charged. The present study highlights the importance of oxygen-assisted γ -CH bond activation for oxygen-containing molecular on Au(111) and provide a new route for the synthesis of ester.

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Introduction

Since Haruta et al. [1] found that gold nanoparticles have an excellent catalytic effect on the oxidation of carbon monoxide at low temperature, the gold catalyst has attracted much attention in environmental chemistry and fine chemical industry. In addition to the low temperature CO oxidation reaction, the gold catalyst in the water gas shift reaction (WGS), alcohol selective oxidation reaction, selective coupling reaction, selective amidation reaction, olefin epoxidation reaction

and nucleophilic addition reaction are all showing high catalytic activity and selectivity at mild reaction conditions [2,3].

In the presence of oxygen or water molecules, oxygen atom can be important intermediates for a variety of transition metal-catalyzed catalytic systems. Madix et al. first discovered that the oxygen atom adsorbed on the surface of the transition metals (copper and silver) of the IB family exhibited the properties of the Brønsted base and promoted the activation of acidic O-H bonds involved in water, methanol and ethanol [4]. Subsequently, more studies have shown that oxygen atoms adsorbed on copper, silver and gold surfaces also

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have a catalytic effect on the oxidation and coupling of alcohols, the oxidation of olefins, and the oxidative dehydrogenation of acids [5]. Similar results indicated that oxygen atom adsorbed on the surface of palladium and platinum can also act as a Brønsted base and promote the oxidation of alcohols and the decomposition of organic acids [6,7]. In recent years, oxygen-assisted selective catalytic reactions on gold surfaces have been extensively studied, including the elective oxidation of olefins, alcohols and amines to produce epoxy compounds, aldehydes or acids and imines, respectively [8], which can also catalyze the oxidative coupling of alcohols to produce esters, or methanol to form amide [9].

Carboxylates can act as important intermediates for the gold surface of the catalytic reaction, mainly because they are intermediate products of the oxidation reaction and may lead to poisoning on the surface of the catalyst. The combination of the carboxylate with the gold surface is very strong and is usually formed by secondary oxidation of an alkane or alcohol. In particular, acetate has been shown to be a non-selectively oxidized intermediate of ethylene on silver surfaces as well as acetaldehyde and ethanol on gold surfaces [10]. Once the carboxylate or similar intermediates are formed, it is possible to reduce the selectivity of the catalyst by blocking the active site [11], thereby preventing the occurrence of the corresponding reaction. In order to control the reaction conditions to avoid the occurrence of these unexpected conditions, it is necessary to understand the stability of the carboxylate salt and its surface reactivity. The basic research on these reactions has led to a greater understanding of the selective control of gold catalysts and the prediction of new reactions, particularly on Au (111) surfaces. In general, the adsorbed oxygen atoms promote the oxidation of the gold surface. Initially, the oxygen atoms exhibit a Brønsted base for H atoms in OH, NH, and even CH groups and form the corresponding activating intermediates and adsorbed OH [12]. For example, ethanol may be present in the pre-adsorbed oxygen atom gold surface generates ethoxy ($C_2H_5O^-$). Next, further activation of the β -CH bond allows the oxidation of ethanol to produce acetaldehyde and ethyl acetate [13].

Experiments conducted by Madix et al. show that the oxygen atoms adsorbed on the gold surface can promote the cleavage of the γ -CH bond in the acetate, while the C-C bond breakage needs to be carried out at higher temperatures [14]. It can be shown that the pre-adsorbed oxygen atoms turn on the new reaction path of the acetate on the Au (111) surface, leading to a selective conversion of the reaction. It is considered that the pre-adsorbed oxygen atoms decrease the stability of the adsorbed acetate on the Au (111) surface [15]. Madix et al. used the programmed temperature response and isotope labeling experiments to provide detailed reaction mechanisms for the decomposition of acetate in the presence of pre-adsorbed oxygen atoms [14], as shown in Scheme 1. Au (111) surface pre-adsorption of oxygen atoms can activate the acetate- γ -CH bond, and then get the product of carbon dioxide and formaldehyde. When the Au (111) surface does not pre-adsorb oxygen atoms, the acetate is broken down into carbon dioxide and methyl by the cleavage of the C-C bond, which in turn binds to the acetate surface of the gold surface to produce methyl acetate. This study demonstrates that pre-adsorbed oxygen atoms play a key role in determining the

reactivity of gold surfaces and propose a method for controlling selectivity in catalytic systems for the formation of carboxylates.

In the theoretical aspect, the density functional theory (DFT) calculations have been performed to study the effect of oxygen species on the A-H bond activation ($A = O, C, N$). The general points gained by the theoretical studies indicated that the effect of oxygen species on the A-H bond is related to electronic structure of catalysts, the alkaline strength of oxygen species as well as the acidic strength of the H atom in A-H [7,15–29]. However, it was found most theoretical works concern A-H bond activation in the simple molecules like CH_4 , H_2O , NH_3 , **very few work on β -CH bond activation [28,29], but no work on γ -CH bond activation induced by the chemisorbed oxygen species to our knowledge.** Based on the mechanism proposed by Madix et al. [14], the decomposition of acetate on the clean and oxygen atom covered Au(111) was simulated by DFT calculations in the present work to elucidate the role of the pre-adsorbed oxygen atoms on the activation of acetate- γ -CH bond from the electronic structure aspect. Moreover, the detailed reaction mechanism of acetate decomposition on Ag(111) was also investigated for a comparison.

Calculation methods and models

Methods Our calculations were performed using the Vienna ab initio simulation package (VASP) [30,31], within the framework of density functional theory (DFT). We utilized the generalized gradient approximation (GGA-PW91) as the exchange-correlation functional [32]. The projector augmented wave (PAW) scheme [33,34] was used to describe the inner cores, and the electronic wave functions were expanded in a plane wave basis with the kinetic cutoff energy of 400 eV. The Brillouin zone sampling was carried out using the $(3 \times 3 \times 1)$ Monkhorst–Pack grids [35]. Dipole corrections for the electric potential and total energy have been applied to eliminate the spurious dipole–dipole interactions along the vertical direction between image super-cells. The transition state (TS) was located by three steps: first, nudged elastic band (NEB) method was employed [36,37] to find out the likely one; second, the atomic structures were relaxed using a quasi-Newton algorithm to make the forces on the atoms are less than $0.035 \text{ eV}/\text{\AA}$; at last, the frequency analysis was performed to confirm the TS. On the basis of the frequency calculation, the zero point energy (ZPE) correction was further performed. The adsorption energy (E_{ads}), the activation energy (E_a) and the total energy change (ΔE) were calculated by the following formulas: $E_{ads} = E_{A/M} - E_A - E_M$, $E_a = E_{TS} - E_{IS}$, and $\Delta E = E_{FS} - E_{IS}$, where $E_{A/M}$, E_M , E_A , E_{TS} , E_{FS} and E_{IS} represent the energies of the adsorbed system, substrate, adsorbed species in the gas phase, TS, FS (final state) and IS (initial state), respectively. Moreover, for the physical adsorption of metal species on the surface (such as carbon dioxide, methyl acetate), we used DFT-D2 method [38] for the van der Waals correction. The Bader charge analysis scheme was performed to investigate the change of electronic structure induced by the oxygen atom [39,40].

Models The model was obtained by cleaving the bulk in the (111) direction, and the Au(111) [Ag(111)] surface was modeled

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