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Crotonaldehyde adsorption on Ir(1 1 1), an interesting *trans*- and *cis*-configuration transformation

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ABSTRACT

Trans- and *cis*-crotonaldehyde (CAL) adsorption behaviors on Ir(1 1 1) were systematically investigated using density functional theory (DFT) method. Our results indicate that the interaction between C=C bond of CAL and Ir(1 1 1) is stronger than that between C=O and surface; and the configurations with both C=O and C=C bonds simultaneously adsorbed at Ir(1 1 1) are more stable than those with an individual C=O or C=C one at surface. It is very interesting to find that the stability of *trans*- and *cis*-CAL on Ir(1 1 1) reverses compared with that in gas phase. On the basis of the potential energy surface (PES) of CAL isomerization, CAL mainly exists as *trans*-structure in gas phase; while *trans*- and *cis*-CAL might coexist on Ir(1 1 1). The electronic interactions between CAL and Ir(1 1 1) are well explained by charge density difference. Different coverages of CAL on Ir(1 1 1) indicates that the interactions between CAL and Ir(1 1 1) decrease with coverage. This work provides important information for the further study of the selective hydrogenation mechanism of CAL.

1. Introduction

α,β-unsaturated alcohol (UOL) is an important type of organic intermediates in fine chemical industry, which has been widely used in production of fragrance and pharmaceuticals [1]. It is generally synthesized by the chemo- and regioselective hydrogenation of corresponding α,β-unsaturated aldehyde (UAL) [2]. According to thermodynamic analysis, it is more favorable for C=C bond hydrogenation than C=O [3]. Furthermore, hydrogenation of α,β-unsaturated aldehyde is a consecutive reaction, which the desired unsaturated alcohol is apt to form saturated alcohol due to further hydrogenation. Therefore, it is a great challenge to develop a catalyst with high hydrogenation activity of UAL and high selectivity of UOL.

Crotonaldehyde (CAL) is a typical representative of UAL, which is widely used as a probe molecule for selective hydrogenation reaction [4]. Noble metals (Pt, Pd, Au, etc.) supported on oxides are generally selected as catalysts for regioselective hydrogenation of CAL [3,5–9]. However, most of them cannot satisfy with the desired high activity and selectivity at the same time.

In order to explore an ideal catalyst, it is necessary to systematically investigate the adsorption, reaction and deactivation behaviors of CAL on the potential catalysts at an atomic level by theoretical method, which might provide important information for catalyst development. Combining experimental and density functional theory (DFT) calculation, Haubrich et al. [10,11] systematically studied the adsorption behaviors on Pt(1 1 1) and Pt–Sn alloy. They found that *trans*- and *cis*-CAL coexist on Pt(1 1 1), and the η^4-di$\sigma_{C=C}$-di$\sigma_{C=O}$ configuration of *trans*-CAL is most stable; electrons of Sn transfer to Pt, which leads to the downshift of d bond center in Pt–Sn alloy. Correspondingly, the adsorption energies of CAL on Pt–Sn alloy decrease by 40–50% compared with those on Pt(1 1 1). Using DFT and microkinetic simulation, Cao et al. [12,13] systematically investigated the adsorption and hydrogenation of CAL on Pt(1 1 1). They suggested that the O_1-C_3-C_4-C_2 hydrogenation path is the dominant channel to form butanol (BOL); meanwhile, butenol (ENOL) produced by 1,4-addition readily tautomerizes to butanal (BAL), leading to the low selectivity of crotyl alcohol (COL). According to the systematic study of acrolein hydrogenation mechanism on Pt(1 1 1), Loffreda et al. [1,14] found that the hydrogenation barrier of C=O bond is lower than that of C=C bond, while the product of C=C hydrogenation is apt to desorption. The selectivity of UOL is determined by the balance between the hydrogenation and desorption of the partially hydrogenated products. Shi et al. [4] systematically calculated the adsorption and reaction of CAL on Pd(1 1 1). They suggested that butanal is produced by the O_1-C_4 hydrogenation of CAL and the sequential isomerization of butenal; the first hydrogenation is the rate

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determined step; low temperature favors the selectivity of α,β-unsaturated alcohol.

Recently, a series of Ir-based catalysts with high activity of CAL and selectivity of crotyl alcohol were developed by Luo's group [15–17]. Compared with much attention upon experimental works, the corresponding theoretical study of α,β-unsaturated aldehyde adsorption on Ir-based catalysts was seldom reported. In the present work, *trans*- and *cis*-CAL adsorption behaviors on Ir(1 1 1) are systematically studied. The electronic interactions between CAL and Ir(1 1 1) are well explained by charge density difference. Furthermore, *trans*- and *cis*-CAL isomerization in gas phase and on Ir(1 1 1) are also compared. This work provides important information for further study of selective hydrogenation mechanism of CAL on Ir-based catalysts.

2. Method and model

All DFT calculations were performed by the Cambridge Sequential Total Energy Package (CASTEP) in Materials Studio Package [18,19]. The ultrasoft pseudopotential with a frozen-core approximation was used for the description of electron–ion interaction [20]. The electron exchange and correlation were treated by the generalized gradient approximation (GGA) [21] using the Perdew–Wang 1991 (PW91) functional [22]. The Kohn–Sham one-electron states were expanded in a plane wave basis with a cutoff energy of 400 eV. The smearing value was set as 0.1 eV. Brillouin zone integration was approximated by a sum over special *k*-points using the Monkhorst–Pack method [23]. The Kohn–Sham equations were solved self-consistently, and the convergence criteria for the energy calculation was set to 2.0×10^{-6} eV/atom; while the maximum force and displacement tolerances of structure optimization was set to 0.05 eV/Å and 5×10^{-3} Å, respectively.

The optimized lattice constant of Ir is 3.908 Å, which is in good agreement with the experimental value, 3.839 Å. Considering the accuracy and efficiency, a four-layer periodic slab of Ir(1 1 1) with the two topmost layers relaxed was adopted in the present work. To eliminate the interactions between CAL, a p($3 \times 2\sqrt{3}$) Ir(1 1 1) superlattice was used in this work. The *k* point was set as $2 \times 2 \times 1$. The vacuum space was set as 12 Å between the slabs to minimize their interaction. Free CAL was optimized in a cubic lattice with the length of 15 Å.

CAL adsorption at different sites on Ir(1 1 1) is systematically studied, and the corresponding adsorption energy is defined as:

$$E_{\mathrm{ads}} = E_{\mathrm{CAL/Ir(1\ 11)}} - (E_{\mathrm{CAL}} + E_{\mathrm{Ir(1\ 11)}}) \qquad (1)$$

where $E_{\mathrm{CAL/Ir(1\,1\,1)}}$ is the total energy of the substrate with CAL; E_{CAL} is the energy of optimized free CAL in a $15 \times 15 \times 15$ Å^3 cube; while $E_{\mathrm{Ir(1\,1\,1)}}$ is the energy of optimized four-layer p($3 \times 2\sqrt{3}$) substrate with the two top layers relaxed. Therefore, a negative value means exothermic adsorption, while a positive one means endothermic adsorption. The more negative the adsorption energy, the stronger the adsorption.

Electronic interactions between CAL and Ir(1 1 1) is analyzed by charge density difference (CDD), which can provide an intuitionistic insight into charge redistribution upon adsorption. CDD is defined as: $\Delta\rho = \rho_{\mathrm{CAL/Ir(1\,1\,1)}} - \rho_{\mathrm{Ir(1\,1\,1)}} - \rho_{\mathrm{CAL}}$, where $\rho_{\mathrm{CAL/Ir(1\,1\,1)}}$ is the charge density of the adsorbed system; while $\rho_{\mathrm{Ir(1\,1\,1)}}$ and ρ_{CAL} are the charge densities of the identical and non-interacting Ir(1 1 1) and CAL extracted from the corresponding adsorbed model CAL/Ir(1 1 1), respectively. The yellow and blue parts represent the electronic accumulation and depletion, respectively.

Transition states (TS) are located by using complete linear synchronous transit (LST) and quadratic synchronous transit (QST) methods [24,25]. LST maximization is performed by an energy minimization in the directions conjugated to reaction pathway, which follows a conjugate gradient minimization. Then, TS approximation is performed by QST maximization, following by another conjugate gradient minimization. The cycles have been repeated until a stationary point is located, which the root mean square force is less than 0.1 eV/Å/atom.

3. Results and discussion

3.1. Trans- and cis-CAL equilibrium composition in gas phase

To obtain the equilibrium composition of *trans*- and *cis*-CALs in gas phase, thermodynamic data are calculated by DFT calculation. The standard molar enthalpy of isomerization of *trans*-CAL into *cis*-CAL is 7.8 kJ/mol, which is well consistent with the experimental value, 7.1 kJ/mol [26] and 8.1 kJ/mol, [27] indicating the reliable theoretical method used in the present work. The corresponding standard molar Gibbs free energy of reaction is 3.16 kJ/mol, which implies the unfavorable isomerization of *trans*-CAL in thermodynamics at 298.15 K.

By calculating the standard molar Gibbs free energy of isomerization at the range of 100–500 K, the corresponding equilibrium constants and composition of *trans*- and *cis*-CALs in gas phase at different temperature are obtained by Eqs. (2) and (3). The corresponding equilibrium composition is shown in Fig. 1. It can be learned from Fig. 1 that equilibrium composition of *cis*-CAL increases as temperature rising. However, *trans*-CAL is the dominant component in the temperature range of 100–500 K. Considering that the hydrogenation temperature of CAL is generally lower than 373.15 K, *cis*-CAL seems negligible for the selective hydrogenation reaction.

$$\mathrm{D_r}G = -RT \ln K_{\mathrm{p}} \qquad (2)$$

$$K_{\mathrm{p}} = \frac{x_{cis\text{-}\mathrm{CAL}}}{x_{trans\text{-}\mathrm{CAL}}} \qquad (3)$$

3.2. Trans-CAL on Ir(1 1 1)

As most of face-centered cubic (fcc) metal, Ir(1 1 1) has the top, bridge (br), fcc and hexagonal-close-packed (hcp) adsorption sites. The possible adsorption terminals of CAL are C=O or C=C bond, or both of them. Combining with possible sites on Ir(1 1 1) and adsorption terminals of CAL, the possible initial configurations are obtained, which will be further geometrically optimized by DFT calculation to obtain stable configurations. The corresponding configurations are defined on the basis of coordination number, bond type formed between CAL and Ir(1 1 1), CAL bond, as well as adsorption site. For example, t-η^5-$\sigma_{\mathrm{C{=}O\text{-}br}}$-$\sigma_{\mathrm{C{=}C\text{-}fcc}}$ represents that

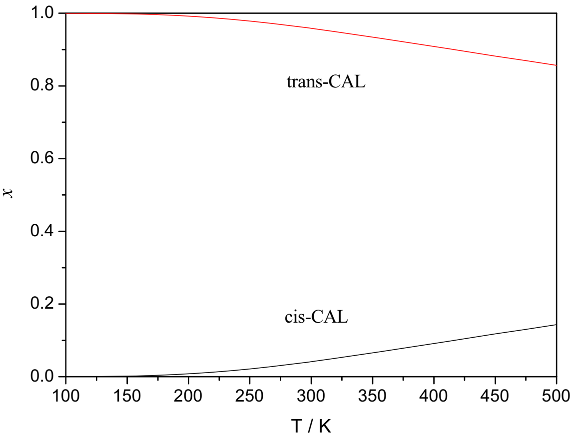

Fig. 1. Equilibrium composition of *trans*- and *cis*-CAL at 100–500 K.