

Catalytic mechanism of Cu (111) surface on the pyrolysis of HFO-1234yf: A density functional study

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ABSTRACT

The catalytic mechanism of Cu(111) surface on the pyrolysis of HFO-1234yf has been investigated by Density Functional Theory (DFT). Firstly, search for the most stable adsorption structure of HFO-1234yf and its pyrolysis products on the Cu(1 1 1) surface. Secondly, The most stable co-adsorption structure of the products of Path1-4 on Cu(1 1 1) surfaces was calculated. Finally, the transition state structure of Path1-4 were investigated. The results prove that the copper surface reduces the energy needed for the pyrolysis of HFO-1234yf.

Keywords: ORC, HFO-1234yf, Material compatibility, Density Functional Theory

1. INTRODUCTION

Organic Rankine Cycle (ORC) is one of the effective ways to recycle low-grade energy. In terms of low-grade energy utilization, ORC has certain advantages over traditional steam cycles in thermal efficiency, variable load capacity and unit capacity. ORC has been widely used in the field of low-grade energy [1-3]. In order to protect the environment, agreements such as the Montreal Protocol and the F gas regulations were formulated to restrict the use of HFCs refrigerants with high GWP (Global Warming Potential) [4, 5]. HFCs widely used in ORC are gradually being replaced by HFOs. HFO-1234yf (ODP=0, GWP₁₀₀=1) is currently the most widely studied HFO refrigerant, with excellent thermodynamic properties, low toxicity, non-flammability, and good environmental performance. It has bright application prospects in refrigeration and air conditioning, heat pumps and organic Rankine cycles.

The operating temperature of the ORC system is much higher than that of the refrigeration system, the

compatibility of organic working fluids and metal materials at high temperatures is an important factor in the selection of materials for the ORC system. The pyrolysis of the working fluid will lead to a decrease in system efficiency and potential safety hazards to the system. Therefore, the thermal stability of the working fluid is a crucial issue for the ORC system. Copper is a common metal material in ORC systems and is often used in high-temperature components. It will be in contact with organic working fluids at high temperatures for a long time in the system. Therefore, copper was selected to study the catalytic mechanism of metal surface on the pyrolysis of HFO-1234yf.

To date, some scholars have conducted research on the compatibility of organic working fluids and metal. Dai et al. [6, 7] explored the compatibility of R245fa, n-pentane and hexamethyldisiloxane with copper. The results indicate that the working fluid interacts with copper. Irriyanto et al. [8] studied the compatibility of 7 alloys with supercritical HFO-1234ze(E). Corrosion has been observed on the surface of copper and bronze. Huo et al. [9] investigated the effect of pure copper on the decomposition of HFO-1336mzz(Z) by density functional theory. The results show that the copper surface has a significant catalytic effect on the pyrolysis of HFO-1336mzz(Z). However, previous studies on the compatibility of HFO working fluids with metal are not comprehensive. HFO-1234yf, as the most promising fourth-generation environmentally friendly refrigerant, Its catalytic mechanism on the copper surface is still lacking. In this study, DFT is used to study the catalytic mechanism of Cu (111) surface on the pyrolysis of HFO-1234yf. This research result has certain guiding significance for the application of HFO working fluid in ORC.

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2. CALCULATION METHODS

A 4×4×3 super-cell was established to simulate Cu (1 1 1) surfaces, with a total of 48 Cu atoms. The bottom two layers of atoms are fixed. The top layer of atoms can move freely. A vacuum layer with a thickness of 15 Å is built on the top to eliminate layer-to-layer interaction. The optimized structure and adsorption sites of the Cu(1 1 1) surface are shown in Fig.1. On the Cu(1 1 1) surface, there are mainly four special adsorption sites: Top, Hcp, Fcc and Bridge.

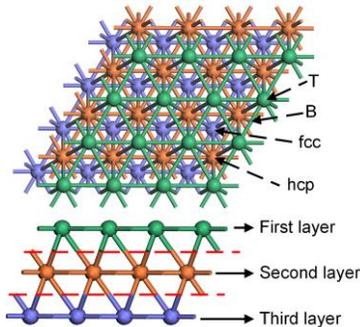


Fig. 1. The optimized structure and adsorption sites of the Cu (1 1 1) surface

All calculations are performed in the Material studio software package, the DMol³ package is selected to calculate all reactants, products and transition states [10, 11]. Structural optimizations adopt density functional theory generalized gradient approximation GGA-PBE exchange correlation function, and perform all-electronic calculations on the dual-value orbital basis set plus orbital polarization function (DNP) level[12]. The Monkhorst-Pack grid parameters in the Brillouin area are set to 3×3×1k, the thermal tail effect is 0.005 Ha to improve the calculation accuracy, calculations take into account the non-restrictive spin. The complete LST/QST method is used to calculate the transition state (TS) of all reaction paths.

The adsorption energy E_{ads} on the copper surface is defined as follows:

$$E_{ads} = E_{adsorbates} + E_{slab} - E_{adsorbates+slab} \quad (1)$$

Among them, $E_{atsorbates}$ represents the energy of the adsorbate, E_{slab} represents the energy of the copper surface, and $E_{atsorbates+slab}$ represents the total energy of the adsorbate and the surface of Cu. E_{ads} as positive means that this adsorbate can be stably adsorbed on the Cu surface.

The reaction energy barrier (E_b) is defined as follows:

$$E_b = E_{TS} - E_R \quad (2)$$

E_{TS} and E_R are the transition state and reactant energy including the copper surface, respectively. At the same time, the bond dissociation energy of the initial reaction of HFO-1234yf without the copper surface is

also calculated, the bond dissociation energy (E_{BDE}) of the initial reaction of HFO-1234yf is defined as follows:

$$E_{BDE} = E_P - E_R \quad (3)$$

E_P and E_R are the energy of the pyrolysis product and reactant of HFO-1234yf, respectively.

3. RESULTS AND DISCUSSION

The top view of Cu(1 1 0) and Cu(1 0 0) can only see two layers of atoms, while the top view of Cu(1 1 1) surface can see three layers of atoms. The adsorption sites on the Cu(111) surface are more abundant. Meanwhile, the Cu(1 1 1) surface is the most stable surface of copper, which has a catalytic effect on many pyrolysis reactions. The Cu(1 1 1) surface is selected to analyze the catalytic mechanism of copper on HFO-1234yf. The energy barriers for the decomposition of the following 4 paths on the surface of Cu(1 1 1) are calculated. Paths 1-4 are the main initial reaction paths of HFO-1234yf [13, 14].



3.1 Adsorption of molecules and radicals

The C atoms in CF₃CF=CH₂ are named C1, C2 and C3 from left to right in order to clearly describe the position of the C atom. The adsorption conditions of the reactants and products of the initial reaction of HFO-1234yf on the 4 adsorption sites on the Cu(1 1 1) surface are all calculated. The most stable adsorption site on the Cu(1 1 1) surface is obtained.

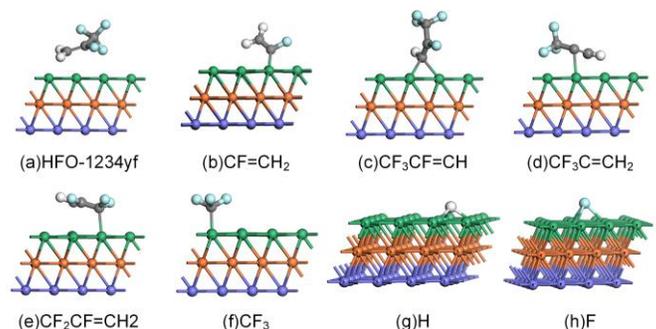


Fig.2. The most stable adsorption structure of HFO-1234yf and its pyrolysis products on Cu(1 1 1) surface

The most stable adsorption structure of HFO-1234yf and its pyrolysis products on Cu(1 1 1) surface is shown in Fig.2. The functional group of HFO-1234yf is a C=C bond, and its most stable adsorption structure is that the C2=C3 bond is adsorbed on the TOP position of the copper surface, C3 is inclined to the copper surface, its adsorption energy is 12.3 kJ·mol⁻¹, as shown in Fig.2(a).

The stable adsorption site of $\text{CF}=\text{CH}_2$ is adsorbed on the Bridge site by C2 atoms, the adsorption energy is $253.6 \text{ kJ}\cdot\text{mol}^{-1}$, as shown in Fig.2(b). The stable adsorption site of $\text{CF}_3\text{CF}=\text{CH}$ is adsorbed on the FCC site by C3 atoms, and the adsorption energy is $153.8 \text{ kJ}\cdot\text{mol}^{-1}$, as shown in Fig.2(c). It is worth noting that after $\text{CF}=\text{CH}_2$ and $\text{CF}_3\text{CF}=\text{CH}$ are stabilized in the adsorption position, their C=C bonds become C-C bonds. The stable adsorption sites of $\text{CF}_3\text{C}=\text{CH}_2$, $\text{CF}_2\text{CF}=\text{CH}_2$ and CF_3 are TOP, which are adsorbed through C2, C1 and C1 respectively. Their adsorption energies are 131.2 , 73.3 and $111.3 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, as shown in Fig.2(d-f). For the two single atoms H and F, the most stable adsorption site Fcc has adsorption energies of 175.9 and $327.5 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, as shown in Fig.2(g-h).

3.2 Co-adsorption of molecules and radicals

The two radicals P1 and P2 generated by the decomposition of HFO-1234yf are modeled according to their most stable adsorption sites in Fig.2. P1 and P2 are placed in adjacent and stable adsorption sites, and stable co-adsorption is obtained after optimization. The most stable co-adsorption structure of the products of Path1-4 on $\text{Cu}(1\ 1\ 1)$ surfaces was calculated.

The co-adsorption energy between free radicals on the Cu surface is defined as follows:

$$E_{\text{co-ads}} = E_{(P1+P2)/\text{slab}} - E_{P1} - E_{P2} - E_{(\text{slab})} \quad (4)$$

Where $E_{(P1)}$, $E_{(P2)}$, $E_{(\text{slab})}$ and $E_{((P1+P2)/\text{slab})}$ are the energy of product A, the energy of product B, the energy of Cu plate and the energy of co-adsorption (A + B) /Cu. The most stable co-adsorption structure on the $\text{Cu}(1\ 1\ 1)$ surface are shown in Fig. 3. These stable co-adsorption structures are considered to be the final state of the decomposition products of HFO-1234yf on the copper surface. Compared with the stable adsorption structure of a single radical, the co-adsorption structure on the $\text{Cu}(1\ 1\ 1)$ surface maintains the original adsorption site. The co-adsorption energies of $\text{CF}_3 + \text{CF}=\text{CH}_2$ and $\text{CF}_3\text{CF}=\text{CH} + \text{H}$ on $\text{Cu}(1\ 1\ 1)$ surface are 470.5 and $302.5 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. $\text{CF}_3\text{C}=\text{CH}_2 + \text{F}$ and $\text{CF}_2\text{CF}=\text{CH}_2 + \text{F}$ both break the C-F bond, but their co-adsorption energies differ greatly, being 119.5 and $618.2 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

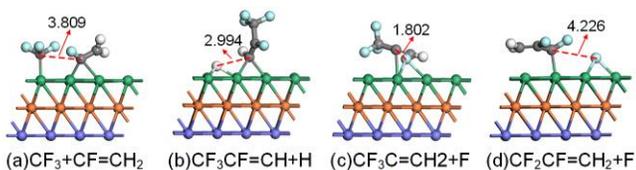


Fig.3. The most stable co-adsorption structure on the $\text{Cu}(1\ 1\ 1)$ surface (unit: Å)

2.3 Pyrolysis of adsorbed HFO-1234yf on Cu surfaces

Fig.4 is the optimized transition state structure of the four initial decomposition reactions of HFO-1234yf on the $\text{Cu}(1\ 1\ 1)$ surface. The energy barriers of the decomposition of HFO-1234yf were calculated on copper and copper-free surfaces to study the catalytic effect of the copper surface on the decomposition of HFO-1234yf. When HFO-1234yf is decomposed on a copper-free surface, Path1-4 only reverses the breakage of the bond, and the bond dissociation energy of Path1-4 is shown in Fig.5(a). When HFO-1234yf decomposes on the copper surface, Path1-4 will break the bond and generate a new bond at the same time. It is necessary to calculate the transition state of the reaction. The energy barrier of Path1-4 is shown in Fig.5(b).

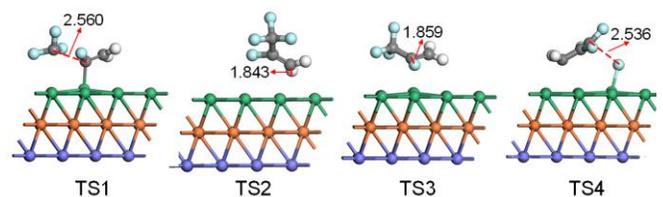
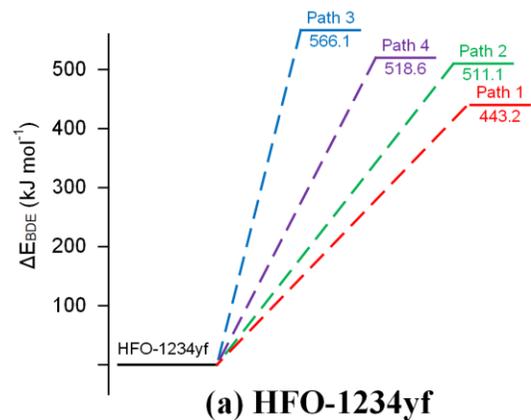
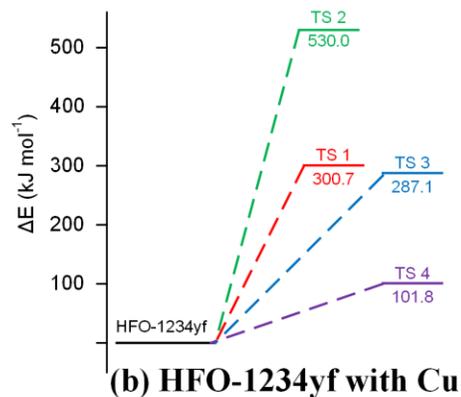


Fig.4. The optimized transition state of HFO-1234yf on the $\text{Cu}(1\ 1\ 1)$ surface



(a) HFO-1234yf



(b) HFO-1234yf with Cu

Fig.5. Energy required for pyrolysis of HFO-1234yf on copper and copper-free surfaces

For path 1, the energy barrier of the copper surface is 67.8% of the bond dissociation energy of the copper-free surface, so the copper surface will greatly promote the occurrence of path 1. For path 2, the bond dissociation energy of the copper surface is increased by 3.7%, so the copper surface has little effect on path 2. For paths 3 and 4, the bond dissociation energy on the copper surface decreased by 49.3% and 44.6%, respectively. Therefore, the presence of the copper surface makes the C-F bond on the C1 atom easier to break. Overall, the presence of copper on the surface will promote the pyrolysis of HFO-1234yf.

4. CONCLUSIONS

The catalytic mechanism of Cu (1 1 1) surface on the pyrolysis of HFO-1234yf was studied by DFT. The main conclusions are as follows:

1) The most stable adsorption structure of HFO-1234yf is that the C2=C3 bond is adsorbed on the TOP position of the copper surface, C3 is inclined to the copper surface.

2) The Cu(1 1 1) surface reduces the energy required to break C-C bonds and C-F bonds, and the Cu surface promotes the pyrolysis of HFO-1234yf.

3) In the future, the compatibility of alloys with working fluids and mixed working fluids will be paid attention to.

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REFERENCE

[1] Uris M, Linares JI, Arenas E. Feasibility assessment of an Organic Rankine Cycle (ORC) cogeneration plant (CHP/CCHP) fueled by biomass for a district network in mainland Spain. *Energy*. 2017;133:969-85.

[2] Van Erdeweghe S, Van Bael J, Laenen B, D'Haeseleer W. Optimal configuration for a low-temperature geothermal CHP plant based on thermoeconomic optimization. *Energy*. 2019;179:323-35.

[3] Freeman J, Guarracino I, Kalogirou SA, Markides CN. A small-scale solar organic Rankine cycle combined heat and power system with integrated thermal energy storage. *Applied Thermal Engineering*. 2017;127:1543-54.

[4] Mota-Babiloni A, Belman-Flores JM, Makhnatch P, Navarro-Esbrí J, Barroso-Maldonado JM. Experimental

exergy analysis of R513A to replace R134a in a small capacity refrigeration system. *Energy*. 2018;162:99-110.

[5] Mota-Babiloni A, Haro-Ortuño J, Navarro-Esbrí J, Barragán-Cervera Á. Experimental drop-in replacement of R404A for warm countries using the low GWP mixtures R454C and R455A. *International Journal of Refrigeration*. 2018;91:136-45.

[6] Dai X, Shi L, An Q, Qian W. Screening of working fluids and metal materials for high temperature organic Rankine cycles by compatibility. *Journal of Renewable and Sustainable Energy*. 2017;9(2).

[7] Dai X, Shi L. Thermal stability and material compatibility for hexamethyldisiloxane as the working fluids of organic Rankine cycle. *Chinese Science Bulletin*. 2019;65(5):410-6.

[8] Irriyanto MZ, Li H-S, Choi B-S, Myint AA, Kim J. Material stability assessment of R-1234ze(E) as a working fluid for supercritical organic Rankine cycle. *Journal of Industrial and Engineering Chemistry*. 2021;96:169-82.

[9] Huo E, Liu C, Xu X, Li Q, Dang C. Dissociation mechanisms of HFO-1336mzz(Z) on Cu(1 1 1), Cu(1 1 0) and Cu(1 0 0) surfaces: A density functional theory study. *Applied Surface Science*. 2018;443:389-400.

[10] Delley B. From molecules to solids with the DMol3 approach. *The Journal of Chemical Physics*. 2000;113(18):7756-64.

[11] Grimme S, Antony J, Ehrlich S, Krieg H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys*. 2010;132(15):154104.

[12] Huo E, Liu C, Xu X, Liu L, Wang S. Dissociation mechanism of HFC-245fa on Cu(1 1 1) surfaces with and without oxygen-covered: A density functional theory study. *Applied Surface Science*. 2019;480:487-96.

[13] Zhang H, Liu C, Xu X, Li Q. Mechanism of thermal decomposition of HFO-1234yf by DFT study. *International Journal of Refrigeration*. 2017;74:399-411.

[14] Irriyanto MZ, Lim H-S, Choi B-S, Myint AA, Kim J. Thermal stability and decomposition behavior of HFO-1234ze(E) as a working fluid in the supercritical organic Rankine cycle. *The Journal of Supercritical Fluids*. 2019;154.