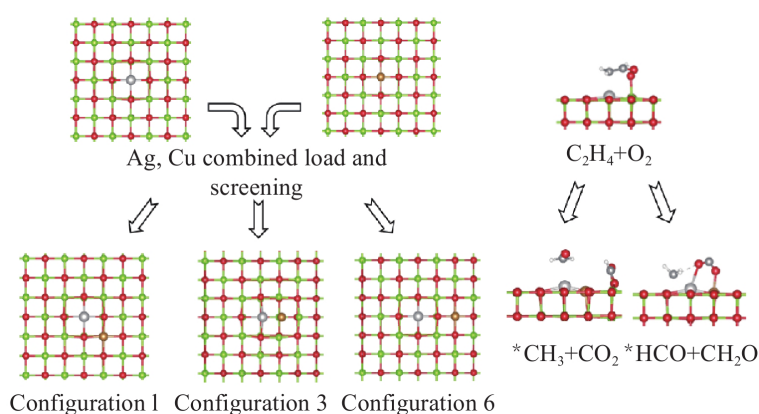


Research on the oxidation mechanism of C_2H_4 in automotive exhaust over MgO-supported Ag-Cu bimetallic synergistic catalysts

ZHANG Wei, ZHAO Genrui, LI Zehong, CHEN Guisheng, CHEN Zhaohui*

Yunnan Provincial Key Laboratory of Internal Combustion Engines, Kunming University of Science and Technology, Kunming 650500, China

Abstract: Ethylene (C_2H_4) in vehicle exhaust is a highly reactive volatile organic compound (VOC). Its photo-oxidative reaction with NO_x contributes to the formation of O_3 and secondary organic aerosols (SOA), the latter being a key precursor of $PM_{2.5}$. In this study, a novel MgO-supported Ag-Cu bimetallic catalyst was designed and investigated using density functional theory (DFT). The effects of Ag and Cu loading on the geometric structure, stability, and reactant adsorption characteristics of the catalyst



were analyzed, and the catalytic oxidation pathways of C_2H_4 over AgCu-MgO was elucidated. The results indicate that loading Ag significantly enhances the adsorption of C_2H_4 . The incorporation of Cu into Ag-MgO to form a AgCu-MgO bimetallic catalyst (dual atom catalyst, DACS) further improves the oxidative activity toward C_2H_4 . Based on the binding energies of the Ag and Cu bimetallic sites and the adsorption energies of C_2H_4 and O_2 , three representative configurations were selected for detailed reaction pathway analysis. Among them, Configuration 6 of AgCu-MgO exhibited the highest catalytic oxidation performance. This study provides new atomic-scale insights for the rational design of efficient catalysts targeting olefinic pollutants in automotive emissions and offers valuable guidance for advancing exhaust after-treatment technologies.

Key words: MgO; Ag-Cu; C_2H_4 ; catalytic oxidation; automotive exhaust

Vehicle exhaust emissions comprise not only conventional pollutants such as CO, HC, NO_x , and particulate matter (PM)^[1–3], but also unconventional species such as C_2H_4 (ethylene)^[4–5]. As a highly reactive volatile organic compound (VOC), C_2H_4 can undergo photochemical reactions with NO_x under sunlight to generate O_3 and secondary organic aerosols (SOA), the latter being a key precursor to $PM_{2.5}$. PM poses serious threats to both human health and atmospheric environmental quality^[6–7]. Therefore, the catalytic removal of olefinic pollutants such as C_2H_4 from vehicle emissions is

essential for meeting increasingly stringent environmental regulations. Currently, noble metal-based oxidation catalysts—such as diesel oxidation catalysts (DOC) and catalyzed diesel particulate filters (CDPF)—exhibit some capability for C_2H_4 removal^[8], yet their efficiency remains limited to approximately 65%^[9]. Noble metals, due to their unsaturated *d*-electron orbitals, possess strong adsorption affinity for reactants and exhibit excellent catalytic performance^[10]. Platinum group metals (PGMs) such as Pt and Pd are particularly effective, as they facilitate the simultaneous adsorption and activation of C_2H_4 and O_2 on

Received: 2025-09-19; Revised: 2025-10-29

Foundation items: Supported by the National Natural Science Foundation of China Project (22362018), the Yunnan Fundamental Research Projects (202401AS070102).

* Corresponding author. E-mail: chen_zhaohuiok@sina.com.

DOI: 10.1016/S1872-5813(26)60640-8 CSTR: 32157.14.2097-213X.2025.JFCT.0197 Associated Data DOI: 10.57760/sciencedb.j00124.00303

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

their surfaces. Huang et al.^[11] reported that Pt-Pd/CeO₂ catalysts show outstanding low-temperature oxidation activity toward HC and CO in diesel exhaust. Huang et al.^[12] found that Pt/ β -zeolite catalysts can achieve up to 90% oxidation efficiency for olefins such as propylene. However, the widespread application of PGMs is constrained by their high cost, scarcity, and susceptibility to sintering and deactivation under high exhaust temperatures^[13–14].

In contrast, Ag is abundant, relatively cost-effective, and demonstrates excellent selective adsorption and oxidation capacity towards C₂H₄, making it a promising alternative for designing efficient and economically viable catalysts. Liang et al.^[15] demonstrated that Ag loading significantly enhances the degradation efficiency of C₂H₄ under light irradiation. Lee et al.^[16] revealed that Ag supported on ZSM-5 zeolite improves the adsorption capacity for C₂H₄. Yan et al.^[17] found that Ag-modified aromatic microporous polyimide (MPI) exhibits enhanced selectivity for C₂H₄ adsorption. Giorgio et al.^[18] also reported that supporting Ag on porous carbon improves the selective adsorption for olefinic species. Furthermore, studies on bimetallic systems have revealed synergistic effects. Pu et al.^[19] investigated Ag-loaded Al₂O₃ modified with various transition metals and concluded that co-loading Ag and Cu results in better selectivity and oxidation performance for C₂H₄ than Ag alone. Greiner et al.^[20] similarly confirmed that Ag-Cu bimetallic catalysts exhibit higher C₂H₄ oxidation selectivity compared to monometallic Ag. While Ag provides strong selectivity and catalytic oxidation capability for C₂H₄, Cu enhances the adsorption of O₂. Therefore, Ag-Cu bimetallic systems are promising for synergistically improving both the selectivity and oxidation activity toward C₂H₄.

Layered double hydroxides (LDHs) are a class of two-dimensional layered clays with a positively charged octahedral structure similar to hydrotalcite. Among them, MgAl-LDHs have attracted widespread attention due to their low synthesis cost and readily available raw materials^[21–23]. Upon high-temperature calcination, MgAl-LDHs are transformed into layered double oxides (MgAl-LDOs) with large specific surface area, high dispersion of active components, and tunable chemical properties. X-ray diffraction (XRD) analysis confirms that the dominant crystalline phase in MgAl-LDO after calcination is MgO^[24–25]. Therefore, in this study, MgO was selected as a simplified structural model of MgAl-LDO to serve as the support of Ag and Cu in the catalytic oxidation of C₂H₄.

To mitigate the adverse effects of C₂H₄ emissions from automobiles on human health and the environment, this study proposes a novel AgCu-MgO catalyst for the catalytic oxidation of C₂H₄. Firstly, density functional theory (DFT) calculations were employed to investigate the effects of Ag and Cu loading on the geometric structure, electronic properties, stability, and adsorption characteristics of MgO. Subsequently, the detailed catalytic oxidation pathways for

C₂H₄ over the Ag- and Cu-modified MgO catalysts were explored. Based on binding energy and adsorption energy analysis, three representative configurations were selected for further evaluation of their reaction pathways. Among them, the optimal catalytic structure was identified. This work provides valuable theoretical insights and design principles for developing efficient catalysts to control olefinic pollutants from automotive exhaust.

1 Computational methods and models

DFT calculations were carried out using the Vienna Ab Initio Simulation Package (VASP)^[26–27]. To accurately describe the interactions between electrons in the catalyst and adsorbates, as well as between electrons and atomic nuclei, the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional^[28] and the projector augmented wave (PAW) method^[29] were employed. A plane-wave cutoff energy of 520 eV was used. Structural relaxations were performed using the conjugate gradient algorithm. The convergence criteria for electronic iterations were set to 1×10^{-5} eV for energy and 0.02 eV/Å for force. Long-range van der Waals interactions, crucial for adsorption and catalytic processes, were corrected using the DFT-D3 dispersion scheme^[30]. The Hubbard U parameter (U-J) was set to 4 eV based on Perdew et al.^[31]. A 3×3 MgO supercell model with a four-layer slab structure was adopted, with the bottom two layers fixed during optimization. A vacuum region of 15 Å was added along the Z-direction to eliminate spurious interactions between adjacent periodic slabs. To improve convergence near the Fermi level, a Gaussian smearing width of 0.05 eV was applied.

The MgO unit cell was optimized using a 6×6×6 Monkhorst-Pack *k*-point mesh. Due to the relatively large size of the supercell, the surface calculations were performed using a 2×2×1 Γ -centered *k*-point mesh. To accurately identify transition states for elementary reactions, the climbing image nudged elastic band (CI-NEB) method^[32] was first employed with a force convergence criterion of 1 eV/Å, allowing for rapid convergence. The resulting transition state structures were subsequently optimized using the improved dimer method (IDM)^[33] until the forces were reduced below 0.05 eV/Å, ensuring precise transition state geometries. Each identified transition state was confirmed by vibrational frequency analysis to possess exactly one imaginary frequency. Gibbs free energies of reactions were calculated using the Vaspkit toolkit^[34], with a reference temperature of 298.15 K. In addition, Bader charge analysis^[35] was conducted to quantify charge transfer during reactions. All structural models and isosurfaces were visualized using the VESTA software package^[36].

The binding energy (E_b) of metal atoms anchored on the MgO surface was calculated as:

$$E_b = E_{\text{cat}} - E_m - E_{\text{sub}} \quad (1)$$

where E_m and E_{sub} represent the energies of the isolated metal atom and the pristine MgO substrate, respectively. A more negative binding energy indicates stronger interaction between the metal atom and the MgO surface.

The adsorption energy (E_{ads}) of a gas molecule on the catalyst surface was calculated as:

$$E_{ads} = E_{tot} - E_{cat} - E_{adsb} \quad (2)$$

where E_{tot} and E_{adsb} represent the total energy of the adsorption system and the energy of the isolated gas molecule, respectively. A more negative value indicates stronger adsorption.

The activation energy (E_b) and reaction energy (ΔE) for an elementary step were defined as:

$$E_b = E_{TS} - E_{IS} \quad (3)$$

$$\Delta E = E_{IM} - E_{IS} \quad (4)$$

where E_{IM} , E_{TS} and E_{IS} represent the energies of the intermediate state, transition state, and initial state along the reaction pathway, respectively.

The temperature-dependent Gibbs free energy change for a reaction step was obtained *via*:

$$G(T) = E + ZPE + \Delta G_{0 \rightarrow T} \quad (5)$$

where $G(T)$ represents the Gibbs free energy at a given temperature T ; E represents the reaction energy associated with reactant and product molecules adsorbed on the catalyst surface at each step of the reaction; ZPE represents the zero-point energy (ZPE) correction; and $\Delta G_{0 \rightarrow T}$ represents the internal Gibbs free energy difference (ΔG) at $T = 298.15$ K.

2 Results and discussion

2.1 Effects of single-atom Ag or Cu loading on the adsorption of C₂H₄ and O₂

In this study, structural optimization was performed on MgO with space group Fm3m(225). The calculated lattice constants are presented in Table 1. The calculated structural parameters are in good agreement with the experimental data in Tang et al.^[37], and also consistent with first-principles DFT results in Filot et al.^[38–39]. The MgO(100) surface exhibited the lowest surface energy (1.30 J/m²), which aligns well with both experimental values^[40–41] and theoretical calculations^[42]. Consequently, a 3×3 MgO(100) surface model was selected all for subsequent computations (Figure 1(a) and 1(b)). The lattice constant was calculated using the following equation:

$$\sigma = \frac{1}{A} \left(\frac{1}{2} (E_{surf} - N_{atoms} \cdot E_{bulk}) + E_{surf}^{rel} \right) \quad (6)$$

where E_{surf} represents the energy of the unrelaxed surface (eV); N_{atoms} represents the total number of atoms in the slab model; A represents the surface area of the slab (Å²); E_{bulk}

represents the energy per atom in the bulk model N_{atoms} (eV); and E_{surf}^{rel} represents the quantity after surface relaxation. A lower surface energy value indicates greater structural stability of the surface.

Loading transition metals can significantly alter the activity, selectivity, and stability of MgO-based catalysts. In this study, Ag and Cu were introduced by substituting a central Mg atom in the surface layer, with the optimized structures shown in Figure 1(c) and 1(d). The binding energies corresponding to Ag-loaded and Cu-loaded configurations were calculated using Eqs (2) and (3), with structural optimizations in Figure 1(a) and 1(b). Four adsorption sites were considered for each metal: the central substitution site (X site), the nearest neighboring Mg site, the nearest O site, and the bridge site between metal and O atoms. For both Ag-MgO and Cu-MgO structures, the calculated binding energies were all negative, indicating that the single-atom loading of Ag or Cu leads to thermodynamically stable catalyst structures. Among these sites, the one yielding the most negative adsorption energy for C₂H₄ and O₂ was identified as the preferred site. In all cases, both C₂H₄ and O₂ molecules tend to adsorb directly above the loaded metal atoms. The corresponding adsorption energies are summarized in Tables 2 and 3.

Table 1 Lattice constants of bulk MgO unit cel

	Lattice parameters $a/\text{\AA}$	
	This work	Experimental
	4.212	4.211 ^[37]
	4.210 ^[38]	
	4.213 ^[39]	

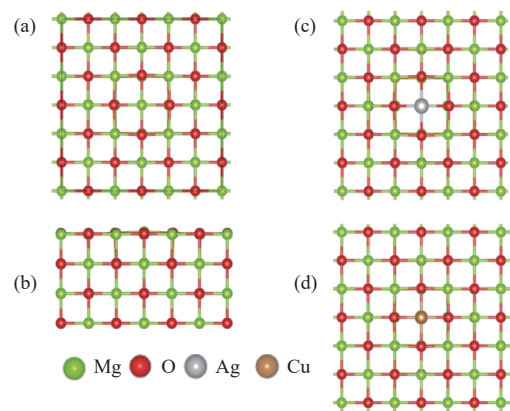


Fig. 1 Optimized structures: (a) top and (b) side views of MgO; (c) Ag-MgO; (d) Cu-MgO

Table 2 Binding energy (eV) and adsorption energy (eV) of C₂H₄ on Ag-MgO and Cu-MgO catalysts

Configuration	E_b/eV	X site	Mg site	O site	Bridge site
Ag-MgO	-6.94	-1.30	-0.27	-0.15	-1.46
Cu-MgO	-7.38	-0.25	-0.35	-0.79	-0.87

Table 3 Binding energy (eV) and adsorption energy (eV) of O₂ on Ag-MgO and Cu-MgO catalysts

Configuration	X site	Mg site	O site	Bridge site
Ag-MgO	-0.17	-0.27	-0.16	-0.45
Cu-MgO	-0.25	-0.32	-0.18	-0.76

For the Ag-loaded MgO(100) model, the adsorption energies at the X site and bridge site were relatively large, with a maximum adsorption energy of -1.46 eV at the bridge site. Compared to the Mg and O sites, C₂H₄ molecules preferentially adsorb near the Ag atom. In contrast, O₂ adsorption on Ag-MgO was much weaker (max -0.45 eV). For Cu-MgO, the bridge site also exhibited the strongest adsorption for C₂H₄, with a maximum adsorption energy of -0.87 eV. However, this adsorption strength was still weaker than the Ag-MgO system. For O₂ adsorption on Cu-MgO, the bridge site again showed the highest affinity, with a maximum adsorption energy of -0.76 eV. These results suggest that Ag loading significantly enhances C₂H₄ adsorption but has a limited effect on O₂, whereas Cu loading moderately improves C₂H₄ adsorption and substantially promotes O₂ adsorption. This complementary behavior suggests that co-loading Ag and Cu could synergistically enhance the adsorption of both C₂H₄ and O₂.

2.2 Effect of dual-atom Ag and Cu loading on adsorption of C₂H₄ and O₂

Co-loading Ag and Cu atoms onto the MgO(100) surface creates dual-atom catalyst (DAC) configurations, where mutual metal-metal interactions must be considered. In this study, 17 AgCu-MgO configurations were constructed (Figure 2). In one set, one of the metal atoms (Ag or Cu) was fixed at an Mg site while the other was placed at a neighboring O site based on spatial proximity. By exchanging the positions of Ag and Cu between the Mg and O sites, 10 configurations were obtained. In another set, by placing both metal atoms at two Mg sites and varying their relative positions, 7 more configurations were generated. All DAC structures were geometrically optimized, and their binding energies were calculated using Eq. (1). The results (Table 4) show that the binding energies of 17 configurations are all negative, confirming their thermodynamic stability.

When both Ag and Cu occupy Mg sites, their binding energies are markedly more negative than those with metals on separate Mg and O sites. This indicates that AgCu-MgO structures with dual-metal atoms anchored at adjacent Mg sites are more thermodynamically stable. Given that Ag exhibited a stronger affinity for C₂H₄ and Cu showed better adsorption of O₂, C₂H₄ preferentially adsorbed near Ag sites, while O₂ favored Cu sites. Structural optimizations were carried out for all configurations, and the corresponding adsorption energies are shown in Figure 3. Compared to the single-atom-loaded MgO structures, most

AgCu-MgO DAC configurations exhibited stronger adsorption capacity for both C₂H₄ and O₂. Among them, Configurations 1 and 6 (both with dual Mg-site metals) showed the strongest adsorption for C₂H₄, with adsorption energies of -1.47 and -1.45 eV, respectively. For O₂, Configuration 3, a single-Mg-site structure with Cu located at an O site, exhibited the highest adsorption energy of -1.27 eV. These results suggest that placing Cu at an O site significantly enhances O₂ adsorption, while the location of Ag (whether at Mg or O site) has a less pronounced effect on C₂H₄ adsorption. To further investigate the effect of atomic positions on catalytic performance, detailed reaction pathway analyses are required. Based on the highest C₂H₄ adsorption energies in the dual-Mg-site configurations (Configurations 1 and 6) and the strongest O₂ adsorption in the single-Mg-site configuration (Configuration 3), these three configurations—all featuring a short Ag-Cu atomic distance—were selected for subsequent mechanistic studies C₂H₄ oxidation.

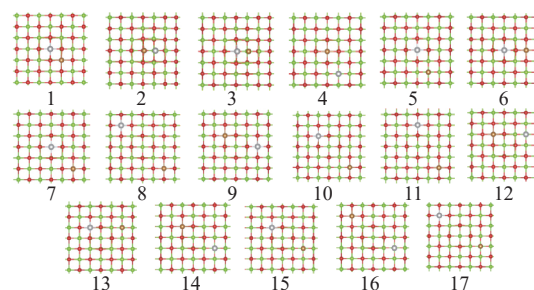
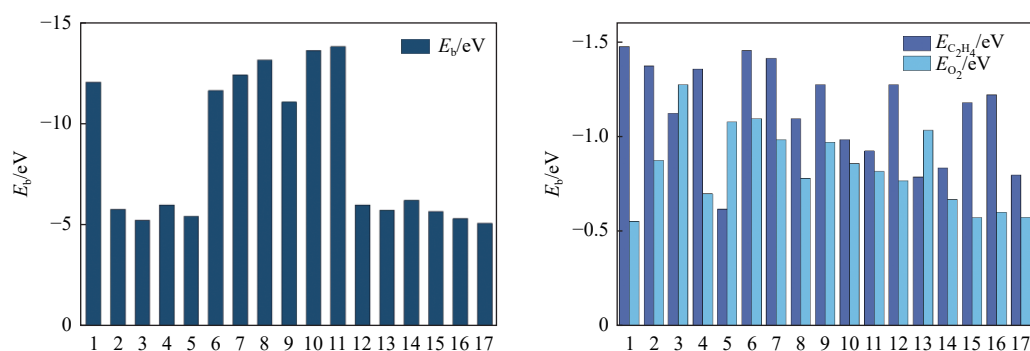


Fig. 2 Top view of 17 configurations of AgCu-MgO dual-atom catalyst

Table 4 Binding energies of 17 configurations of AgCu-MgO

AgCu- <i>n</i>	<i>E_b</i> /eV	<i>E_{C₂H₄}</i> /eV	<i>E_{O₂}</i> /eV
Config. 1	-12.01	-1.47	-0.55
Config. 2	-5.68	-1.37	-0.87
Config. 3	-5.13	-1.12	-1.27
Config. 4	-5.89	-1.36	-0.69
Config. 5	-5.32	-0.61	-1.07
Config. 6	-11.59	-1.45	-1.09
Config. 7	-12.37	-1.41	-0.98
Config. 8	-13.11	-1.09	-0.78
Config. 9	-11.02	-1.27	-0.97
Config. 10	-13.58	-0.98	-0.86
Config. 11	-13.78	-0.92	-0.81
Config. 12	-5.89	-1.27	-0.76
Config. 13	-5.62	-0.78	-1.03
Config. 14	-6.12	-0.83	-0.67
Config. 15	-5.57	-1.18	-0.57
Config. 16	-5.21	-1.22	-0.60
Config. 17	-4.97	-0.79	-0.57


 Fig. 3 Binding energies and adsorption energies of C_2H_4 and O_2 of 17 configurations of AgCu-MgO

2.3 Oxidation pathway analysis of selected AgCu-MgO configurations toward C_2H_4

The oxidation pathways of C_2H_4 on Configurations 1, 3 and 6 were analyzed in detail. Due to its high molecular symmetry, the four hydrogen atoms in C_2H_4 molecule are equivalent in both spatial configuration and chemical reactivity. As a result, each hydrogen exhibits similar behavior in dehydrogenation reactions, limiting C_2H_4 to only two reactive sites for initial oxidation. Following the abstraction of one hydrogen atom, C_2H_4 forms a highly reactive vinyl radical ($C_2H_3\cdot$), which undergoes a barrierless addition reaction with O_2 to form a peroxy radical intermediate ($C_2H_3O_2\cdot$). This addition step is considered as a key intermediate process in the catalytic oxidation of C_2H_4 ^[5]. Additionally, O_2 can directly add across the C=C double bond. Electrostatic potential (ESP) analysis indicates that this site exhibits strong electrophilic character, facilitating the formation of a dioxetane-like intermediate ($C_2H_4O_2$). Both reaction sites were considered in this study. For each of the three selected configurations, three possible oxidation pathways were proposed based on these initial activation modes, resulting in a total of nine reaction pathways. Figure 4 presents the top and side views of the molecular structures for key states in these pathways.

Pathway 1 for Configurations 1, 3 and 6 is depicted in the Gibbs free energy diagram in Figure 5. In Configuration 1, C_2H_4 first adsorbs near the Ag atom, forming the intermediate CS3. Subsequently, O_2 adsorbs on the Mg region of the surface, initiating a Langmuir-Hinshelwood (L-H) type oxidation. In this pathway, co-adsorbed O_2 reacts with the adsorbed C_2H_4 to form the $C_2H_3O_2$ intermediate. This intermediate then undergoes lateral rotation, with one O atom bonding to the Cu site near the vinyl group and the other to the Ag site, resulting in the formation of CS4. The ΔG for the $CS3 + O_2 \rightarrow CS4$ step in Configuration 1 is relatively small, only 0.09 eV. For Configuration 6, the ΔG for the same step is 0.26 eV, while in Configuration 3, the $CS3 \rightarrow CS4$ transition exhibits a negative ΔG of -0.61 eV. This enhanced thermodynamic favorability in Configuration 3 is attributed to the positioning of Cu at an O site, which enhances electron donation and strengthens O_2 adsorption.

For all three configurations (1, 3 and 6), the transformation of CS4 to CS5 is exothermic. This step involves the formation of a three-membered ring peroxide intermediate (CS5). The energy release is substantial for Configurations 1 ($\Delta G = -3.52$ eV) and 3 ($\Delta G = -3.73$ eV), but minimal for Configuration 6 ($\Delta G = -0.05$ eV).

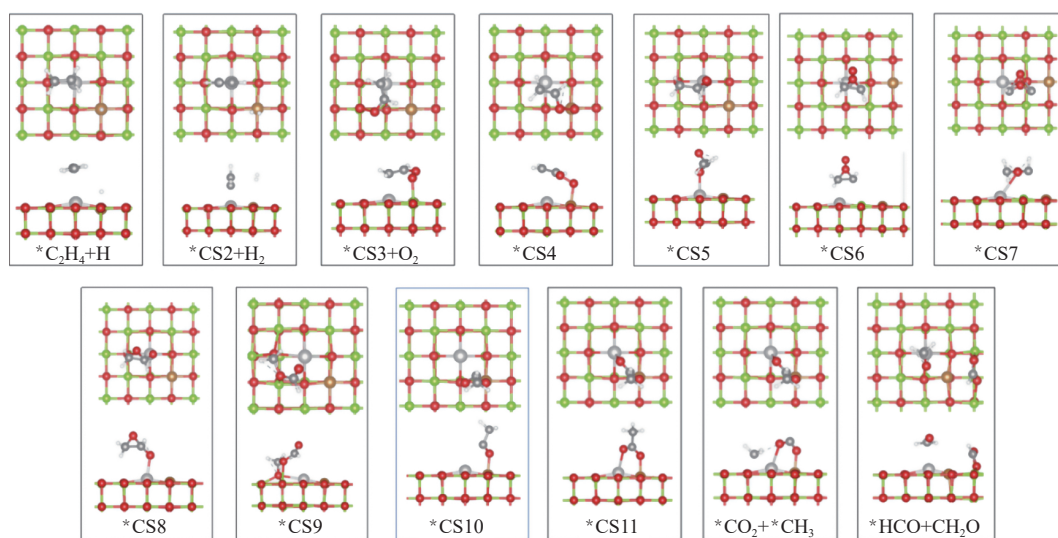


Fig. 4 Top and side views of reaction state structures of reaction Pathway 3

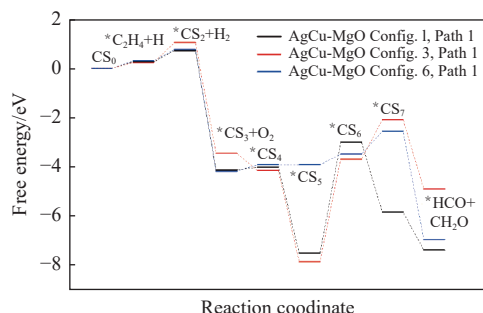


Fig. 5 Free energy step diagram for Pathway 1 of C_2H_4 oxidation reaction on AgCu-MgO Configurations 1, 3, 6

In Configuration 1, the $CS_5 \rightarrow CS_6$ transformation is the rate-determining step for Pathway 1, with a high energy barrier of 4.33 eV. In contrast, for Configuration 6, this step has a lower barrier, making the later $CS_6 \rightarrow CS_7$ step ($\Delta G = 0.94$ eV) rate-limiting. This latter step involves the cleavage of the $C=C$ bond in C_2H_4 , yielding $*HCO$ and CH_2O intermediates.

Figure 6 depicts the Gibbs free energy profile for Pathway 2 of C_2H_4 oxidation on Configurations 1, 3 and 6. For Configuration 1, the $CS_5 \rightarrow CS_8$ step is the rate-determining step, with a ΔG of 2.17 eV, which is significantly lower than the 3.52 eV barrier observed for the $CS_5 \rightarrow CS_6$ step in Pathway 1. This suggests that Configuration 1 more readily proceeds through Pathway 2 to form $*HCO$ and CH_2O intermediates. For Configuration 3, both the $CS_5 \rightarrow CS_8$ and $CS_8 \rightarrow CS_9$ steps present high barriers (2.20 and 3.49 eV, respectively), rendering Pathway 2 less likely. For Configuration 6, the rate-determining step for Pathway 2 is $CS_8 \rightarrow CS_9$, which exhibits a ΔG of 2.96 eV—significantly higher than the 0.94 eV barrier of the $CS_6 \rightarrow CS_7$ step in Pathway 1. Therefore, for Configuration 6, Pathway 1 is the preferred route.

Figure 7 illustrates Pathway 3 for the formation of $*CH_3$ and CO_2 from C_2H_4 on Configurations 1, 3 and 6. In this pathway, the key intermediate CS_5 undergoes O–O bond cleavage followed by oxygen migration, ultimately breaking the $C=C$ bond, resulting in the formation of $*CH_3$ and CO_2 . For Configurations 1 and 3, the $CS_5 \rightarrow CS_{10}$ step is rate-determining, with ΔG values of 2.08 and 2.21 eV, respectively. For Configuration 6, the rate-limiting step occurs earlier ($CS_3 \rightarrow CS_4$) with a much lower ΔG of 0.32 eV.

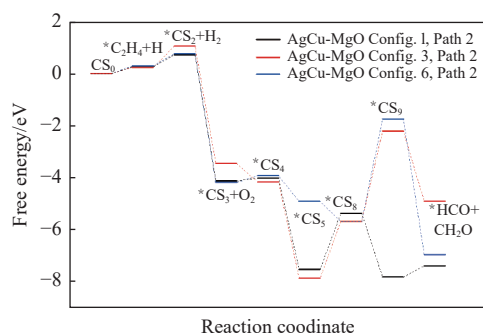


Fig. 6 Free energy diagram for Pathway 2 of C_2H_4 oxidation reaction on AgCu-MgO Configurations 1, 3, 6

These results suggest that the AgCu-MgO catalyst facilitates $*CH_3$ formation during C_2H_4 oxidation, with Configuration 6 demonstrating the most favorable catalytic performance among the three. The $*CH_3$ radical is relatively stable, and further cleavage of its $C-H$ bond requires a considerably higher activation energy. In this study, the Ag-Cu dual sites are highly effective in activating O_2 and initiating its reaction with C_2H_4 . However, the reactivity and quantity of surface O species (e.g., O or OH) generated under these conditions may be insufficient for the efficient low-temperature cleavage of the stronger $C-H$ bonds in $*CH_3$.

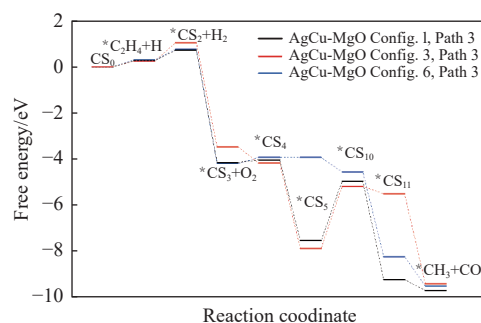


Fig. 7 Free energy step diagram for Pathway 3 of C_2H_4 oxidation reaction on AgCu-MgO Configurations 1, 3, 6

3 Conclusions

To investigate the influence of Ag and Cu loading on the C_2H_4 oxidation performance of MgO-based catalysts, this study performed a systematic DFT investigation of MgO, Ag-MgO, Cu-MgO and 17 different DAC configurations with Ag and Cu co-loaded at various sites on MgO(100) surface. The reaction mechanisms of C_2H_4 oxidation over the selected AgCu-MgO configurations were explored through DFT calculations. The main conclusions are summarized as follows:

Loading Ag onto the MgO(100) surface significantly enhances C_2H_4 adsorption, resulting in a maximum adsorption energy of -1.46 eV. However, its capacity for O_2 adsorption is considerably weak (-0.45 eV). Conversely, Cu-loaded MgO exhibits a moderate affinity for C_2H_4 (-0.87 eV at the bridge site) but a higher adsorption energy for O_2 (-0.76 eV), outperforming Ag-MgO system in O_2 adsorption.

Among the 17 modeled AgCu-MgO DAC configurations, structures where both Ag and Cu atoms are co-adsorbed at Mg sites are thermodynamically more stable (binding energies below -10 eV) than those with the metals at Mg and O sites. In particular, DAC configurations with Ag and Cu atoms in close proximity generally exhibit enhanced co-adsorption capabilities for both C_2H_4 and O_2 . Notably, positioning Cu at an O site significantly increases O_2 adsorption energy.

On the AgCu-MgO surface, C_2H_4 oxidation preferentially proceeds through $C=C$ bond cleavage, leading to the formation of $*CH_3$ and CO_2 . For all three selected

configurations (1, 3, and 6), the free energy barriers associated with the rate-limiting steps in the *HCO and CH₂O formation pathway are consistently higher than those for the *CH₃ and CO₂ pathway. Among them, Configuration 6 exhibits the lowest energy barrier (0.32 eV) for its rate-limiting step in Pathway 3, indicating it as the most promoting structure for catalyzing C₂H₄ oxidation toward *CH₃ and CO₂ formation.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] YU W, ZHAO F, YANG W, et al. Integrated analysis of CFD simulation data with K-means clustering algorithm for soot formation under varied combustion conditions[J]. Appl Therm Eng, 2019, 153: 299–305.
- [2] WANG Y, CHUNG S H. Soot formation in laminar counterflow flames[J]. Prog Energy Combust Sci, 2019, 74: 152–238.
- [3] JOHANSSON K O, HEAD-GORDON M P, SCHRADER P E, et al. Resonance-stabilized hydrocarbon-radical chain reactions may explain soot inception and growth[J]. Science, 2018, 361(6406): 997–1000.
- [4] HOU X N, WANG J, SONG C B, et al. Research status and trends of unconventional pollutant emissions from diesel engines[J]. Chin Agric Mech, 2020, 41(1): 126.
- [5] WANG Y C, DAI G L, GENG Z Y, et al. DFT study on the reaction of ethylene radical with ozone[J]. Acta Phys-Chim Sin, 2004, 20(9): 1071–1077.
- [6] KIRMAN C R, NORTH C M, TRETYAKOVA N Y, et al. Use of biomarker data and metabolite relative potencies to support derivation of noncancer reference values based on the reproductive and developmental toxicity effects of 1, 3-butadiene[J]. Regul Toxicol Pharm, 2022, 134: 105239.
- [7] VALDEZ-FLORES C, ERRAGUNTLA N, BUDINSKY R, et al. An updated lymphohematopoietic and bladder cancers risk evaluation for occupational and environmental exposures to 1, 3-butadiene[J]. Chem Biol Interact, 2022, 366: 110077.
- [8] ZHANG W, SONG C L, LI F C, et al. Study on aldehyde and ketone emissions from ethanol-diesel blend fuels[J]. Trans CSICE, 2008, 28(2): 238–242.
- [9] WEI H, YAO C. Comparison of the conversion efficiency of DOC and DPOC to unregulated emissions from a DMDF engine[J]. Fuel, 2017, 204: 71–84.
- [10] MEDFORD A J, VOJVODIC A, HUMMELSHØJ J S, et al. From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis[J]. J Catal, 2015, 328: 36–42.
- [11] HUANG H F, WANG L Y, et al. Activity and sulfur resistance of Pt-Pd/CeO₂ catalyst for diesel oxidation catalyst (DOC)[J]. J Fuel Chem Technol, 2013, 41(11): 1401–1408.
- [12] HUANG P, CHEN Y D, LAI N J, et al. Effect of different metal modifications on the oxidation performance of Pt/β-zeolite for HC, CO and SO₂ in diesel exhaust[J]. J Fuel Chem Technol, 2016, 44(7): 882–887.
- [13] CHEN W Q. Study on simultaneous removal of soot and nitrogen oxides from diesel engine exhaust by lanthanum-manganese perovskite catalysts[D]. Guangzhou: South China University of Technology, 2020.
- [14] DAI F F. Study on Co- and Mn-based oxide catalysts for catalytic purification of diesel vehicle exhaust[D]. Tianjin: Tianjin University, 2014.
- [15] LIANG X Z, WANG P. Adsorption of gaseous ethylene via induced polarization on plasmonic photo catalyst Ag/AgCl/TiO₂ and subsequent photo degradation[J]. Appl Catal B: Environ, 2020, 220: 356–361.
- [16] LEE J, GIEWONT K, CHEN J. Ag/ZSM-5 traps for C₂H₄ and C₂H₆ adsorption under cold-start conditions[J]. Microporous Mesoporous Mater, 2021, 327: 111428.
- [17] YAN J, ZHANG B. Highly selective adsorption for ethylene, propylene, and carbon dioxide in silver-ionized microporous polyimide[J]. J Phys Chem C, 2019, 123: 575–583.
- [18] DE LUCA G, SAHA D, CHAKRABORTY S. Why Ag(I) grafted porous carbon matrix prefers alkene over alkane? An inside view from ab-initio study[J]. Microporous Mesoporous Mater, 2021, 316: 110940.
- [19] PU T, TIAN H, GIEWONT K. Overview of selective oxidation of ethylene to ethylene oxide by Ag catalysts[J]. ACS Catal, 2019, 9: 10727–10750.
- [20] GREINER M, CAO J. Phase coexistence of multiple copper oxides on AgCu catalysts during ethylene epoxidation[J]. ACS Catal, 2018, 8(3): 2286–2295.
- [21] JABŁOŃSKA M, PALKOVITS R. Nitrogen oxide removal over hydrotalcite-derived mixed metal oxides[J]. Catal Sci Technol, 2018, 6: 49–72.
- [22] ALMEIDA M F, BELLATO C R, MIRANDA L D, et al. Preparation of calcined hydrotalcite/TiO₂-Ag composite and enhanced photocatalytic properties[J]. Ceram Int, 2017, 43(2): 1843–1852.
- [23] YUWEN X M, FENG W S, MU X L, et al. Green synthesis of Mg-Al hydrotalcite-based catalysts for the preparation of ethyl methyl carbonate[J]. J Fuel Chem Technol, 2024, 52(11): 1652–1663.
- [24] LI Z, HONG R, ZHANG Z, et al. Single-atom catalysts in environmental engineering: Progress, outlook and challenges[J]. Molecules, 2023, 28(9): 3865.
- [25] YU H, LI F S, ZHU X, et al. Ce-Fe-Zr-O/MgO monolithic oxygen carriers for chemical looping partial oxidation of methane to syngas[J]. J Fuel Chem Technol, 2015, 43(4): 499–506.
- [26] XIANG N, HAN X, BAI Y, et al. Size effect of γ-Al₂O₃ supports on the catalytic performance of Pd/γ-Al₂O₃ catalysts for HCHO oxidation[J]. Mol Catal, 2020, 494: 111112.
- [27] HE M, CAO Y, JI J, et al. Superior catalytic performance of Pd-loaded oxygen-vacancy-rich TiO₂ for formaldehyde oxidation at room temperature[J]. Journal of Catalysis, 2021, 396: 122–135.
- [28] ROJAS H A, LÓPEZ V P, BRIJALDO M H, et al. Effect of boron on the surface properties of nickel supported on hydrotalcite-type mixed oxides in methanol decomposition[J]. Molecular Catalysis, 2020, 498: 111262.
- [29] SUN Y, YIN W M, WANG Y, et al. Fabrication of ultra-thin MgAl layered double oxide by cellulose templating and its immobilization effect toward heavy metal ions: Cation-exchange and deposition mechanism[J]. Chem Eng J, 2022, 427: 132017.
- [30] KRESSE G, FURTHMÜLLER J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set[J]. Comput Mater Sci, 1996, 6(1): 15–50.
- [31] PERDEW J P, BURKE K, ERNZERHOF M. Generalized gradient approximation made simple[J]. Phys Rev Lett, 1996, 77(18): 3865.
- [32] BLOCH P E. Projector augmented-wave method[J]. Phys

- Rev B, 1994, 50(24): 17953.
- [33] KRESSE G, JOUBERT D. From ultrasoft pseudopotentials to the projector augmented-wave method[J]. Phys Rev B, 1999, 59(3): 1758.
- [34] GRIMME S, ANTONY J, EHRLICH S, et al. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu[J]. J Chem Phys, 2010, 132: 154104.
- [35] LAKSHMY S, KUNDU A, KALARIKKAL N, et al. Pd-functionalized 2D TMDC $MoTe_2$ monolayer as an efficient glucose sensor: A first-principles DFT study[J]. Appl Surf Sci, 2023, 631: 157525.
- [36] HENKELMAN G, UBERUAGA B P, JONSSON H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths[J]. J Chem Phys, 2000, 113(22): 9901–9904.
- [37] TANG W, SANVILLE E, HENKELMAN G. A grid-based Bader analysis algorithm without lattice bias[J]. J Phys Condens Matter, 2009, 21(8): 084204.
- [38] FILOT I A W, ZIJLSTRA B, HENSNE E J M. MKMCXX. A C++ program for constructing microkinetic models[CP]. <http://www.mkmcxx.nl>.
- [39] FILOT I A W, VAN SANTEN R A, HENSEN E J M. The optimally performing Fischer–Tropsch catalyst[J]. Angew Chem Int Ed, 2014, 53(47): 12746–12750.
- [40] DENG J, SONG W, JING M, et al. A DFT and microkinetic study of HCHO catalytic oxidation mechanism over Pd/Co_3O_4 catalysts: The effect of metal-oxide interface[J]. Catal Today, 2020, 339: 210–219.
- [41] HUANG J, LI X, WANG X, et al. New insights into CO_2 methanation mechanisms on Ni/MgO catalysts by DFT calculations: Elucidating Ni and MgO roles and support effects[J]. J CO_2 Util, 2019, 33: 55–63.
- [42] BAI M, SONG Z, YANG Z, et al. Catalytic conversion mechanism of guaiacol as the intermediate of lignin catalytic pyrolysis on MgO surface: Density functional theory calculation[J]. J Mol Liq, 2023, 369: 120920.

MgO 负载 Ag-Cu 双金属协同对汽车尾气中乙烯的氧化机制研究

张 韦，赵根锐，李泽宏，陈贵升，陈朝辉*

(昆明理工大学 云南省内燃机重点实验室, 云南 昆明 650500)

摘 要: 汽车尾气中的乙烯 (C_2H_4) 是一种高活性 VOCs, 受光照可与 NO_x 反应生成 O_3 和二次有机气溶胶 (SOA), 而 SOA 是 $PM_{2.5}$ 的重要前体物, PM 则会危害人体健康和大气环境。本工作基于密度泛函理论 (DFT), 设计 MgO 负载 Ag-Cu 双金属的新型催化剂, 并分析 Ag、Cu 负载对催化剂几何结构、稳定性、反应物吸附特性的影响, 进而探究 AgCu-MgO 的 C_2H_4 催化氧化性能。研究表明, 负载 Ag 能有效提升催化剂的 C_2H_4 吸附性。在 Ag-MgO 的基础上负载 Cu, 构成 AgCu-MgO 双金属催化剂 (DACS) 则能提高对 C_2H_4 的氧化性。通过分析催化剂的 Ag、Cu 双金属负载结合能, 以及对 C_2H_4 、 O_2 的吸附能, 筛选三种构型进行 C_2H_4 催化氧化路径计算。其中, AgCu-MgO 构型 6 表现出最优的 C_2H_4 氧化性能。本研究可为汽车排放烯烃类污染物的氧化型催化剂设计提供新思路, 并对汽车后处理技术的开发具有重要参考价值。

关键词: MgO; Ag-Cu; C_2H_4 ; 催化氧化; 汽车尾气

中图分类号: TK421, O643.3

文献标识码: A

作者简介:



张韦(1979), 博士/教授, 研究方向为汽车污染物控制关键技术研究、新型车用碳中和燃料开发等, koko_575@aliyun.com。



陈朝辉(1980), 博士/教授, 研究方向为汽车污染物控制关键技术研究、新型车用碳中和燃料开发等, chenzhaozhao@sina.com。