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Promotion effect of epoxy group neighboring single-atom Cu site on acetylene hydrochlorination

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ABSTRACT

Carbon materials have been used as the support for catalysts in the field of acetylene hydrochlorination, the influence of inevitable oxygen-containing moieties on the reaction is often ignored and the mechanism of the oxygen-doping structure remains ambiguous. Herein, we explored the effect of the oxygen-containing group (C–O–C) in the support on the activity of single-atom dispersed Cu catalysts. By immersing the Cu single-atom catalyst in an alkaline solution, the epoxy species on the carbon support was cleaved to obtain a pure ether species while the Cu site was modified to a more electron-deficient state. The turnover frequency value of Cu/O-FLP catalyst with epoxy groups was 1.6-fold higher than that of alkaline treated catalyst. Our result indicated that the epoxy groups could assist adjacent single-atom Cu sites to synergistically promote the adsorption and cleavage of the reactant hydrogen chloride toward form C–OH and Cu–Cl bonds, and reduce the reaction energy barrier. The presence of electron deficient Cu sites and ether species could induce competitive adsorption of the acetylene and hydrogen chloride, thereby reducing the activity of the catalyst. This study highlights the influence of surface oxygen species and the tunability of the support, providing the foundation for the fabrication of higher-activity Cu catalysts for acetylene hydrochlorination.

The hydrochlorination of acetylene is a crucial technology for the industrial production of vinyl chloride monomer *via* activated carbon-supported mercury chloride ($HgCl_2$/AC) catalyst. However, the environmental issues brought about by the mercury catalysts has urgently needed to be addressed, and exploring mercury-free catalysts is the only way to promote sustainable development [1–3]. The Cu-based catalysts are the most promising alternatives for mercury-free catalyst due to their affordability and good initial catalytic activity toward acetylene hydrochlorination reaction. However, the application of Cu-based catalysts is limited by the aggregation of active centers and the reduction of high valence states in metallic copper, and researchers have been committed to improve catalytic activity and stability [4,5]. Among them, atomically dispersed Cu catalysts not only maximize the utilization of metal sites but also contribute to regulate the catalytic active site and investigate reaction mechanisms [6–12].

It is known that the support of single-atom Cu catalyst can be modified by the doping of heteroatom such as nitrogen [13–17] and phosphorus [9,18,19] on carbon materials to improve the catalytic performance. However, the surface oxygenated groups on carrier are inevitable in carbon materials, and there is a certain correlation between the improvement of catalytic activity and the content of surface functional groups such as phenols, ethers, and carbonyls [20–22]. Li *et al.* proposed that the carbonyl groups on the carbon support could enhance the stability of atomically dispersed $AuCl_x$ active species and improve catalytic performance [23]. Hutchings *et al.* used the oxidized carbon supports to study the correlation between the degree of oxygen concentration on the carbon support and its catalytic activity, and found that increasing the relative concentration of C–O groups is a key descriptor for improving low-temperature activity of Au-based catalyst [24]. The above studies suggested the O-containing functional groups can efficiently tuning the activity of metal catalyst, but the role of oxygen-containing groups on carbon support for single atom active

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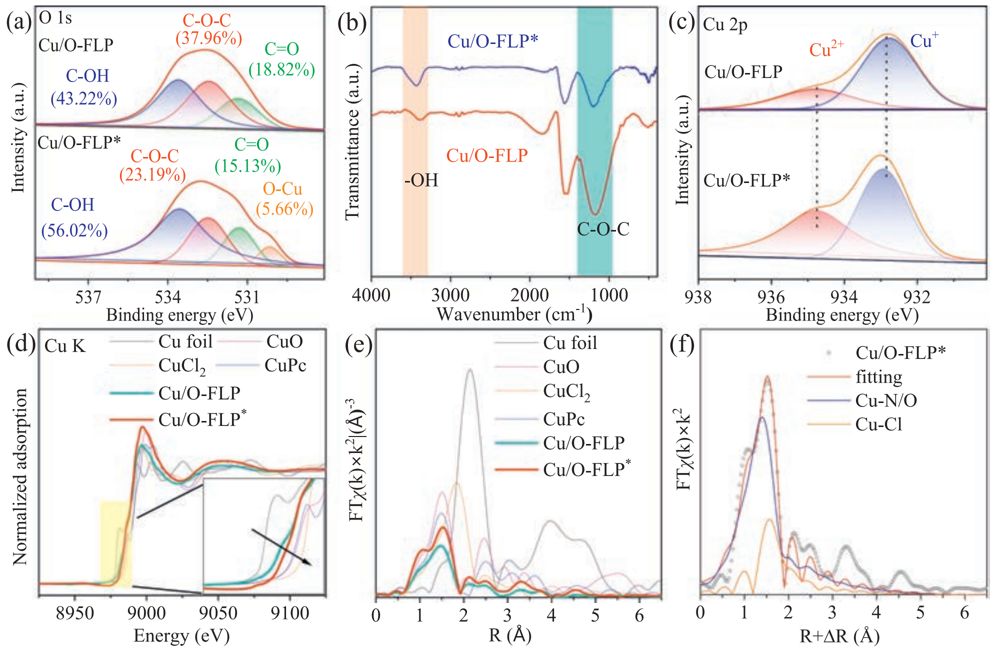

Fig. 1. The structural modulation of Cu/O-FLP and Cu/O-FLP* catalysts. (a) The O 1s XPS spectra, (b) FT-IR spectra, and (c) the Cu 2p XPS spectra of Cu/O-FLP and Cu/O-FLP*. (d) The Cu K-edge XANES spectra and (e) Fourier transform of the k^2-weighted χ-EXAFS data of Cu/O-FLP and Cu/O-FLP*. (f) EXAFS fitting result at R space of Cu/O-FLP*.

sites is still unclear. Systematic research on it is of great significance for studying the catalytic mechanism of acetylene hydrochlorination reaction at the atomic level and guiding the design of efficient catalysts.

Our previous studies have pointed out the importance of epoxy groups (C–O–C) in the hydrochlorination reaction of acetylene, the epoxide group acted as additional active sites to activate and cleave reactant, giving rise to the C–O–H$^{\delta+}$ species during HCl pre-activation [7]. The preferential HCl activation forms the saturated six-coordination configuration of the single-atom Cu center, which effectively suppressing the formation of explosive copper acetylide. Nevertheless, the C–O–C in the carbon supports does not consist entirely of epoxy groups and it is unclear whether the ether species contained in it play the catalytic role. Due to the relatively stable character of ethers, their epoxy groups tend to induce ring cleavage reaction under acidic or alkaline conditions [25,26], while the reactant hydrogen chloride in acetylene hydrochlorination could play a role in ring opening. In this regard, we consider opening the rings of epoxy groups under alkaline conditions to probe the adsorption and dissociation of HCl by epoxy and ether species.

Here we utilized impregnation with an alkali solution to induce the cleavage of epoxy groups on the single-atom Cu catalyst supports. Experimental characterization confirmed the presence of only a sole ether species in the C–O–C on the support surface after impregnation, and that the electronic structure of the Cu atoms was modulated. The Cu/O-FLP catalyst with epoxy group exhibited much superior acetylene hydrochlorination performance than Cu/O-FLP* with a single ether group. The reason for the difference in activity was investigated by HCl activation of the catalysts, and it was found that the coupling of the epoxy groups to the Cu sites synergistically promoted the adsorption and dissociation of hydrogen chloride, effectively reducing the reaction energy barriers. The existence of ether species with Cu sites induced competitive adsorption between the reactants acetylene and HCl, resulting in a reduction in the reaction rate. This work will elucidate the impact of C–O–C oxygen-containing groups on the adsorption of reactants to the catalyst support and open an avenue for designing high-performance catalysts.

Based on our previous research work, we have prepared frustrated single-atom Cu/O Lewis pair site catalyst (Cu/O-FLP) with epoxy group around single-atom sites. Due to the relative instability of epoxy group compared to ether, which were prone to undergo ring cleavage with acid/base, we employed an alkaline solution to impregnate the catalyst for eliminating the epoxy group (Cu/O-FLP*). The chemical states of the as-prepared samples were firstly studied by X-ray photoelectron spectroscopic (XPS). As shown in Fig. 1a, the high-resolution O 1s XPS spectra showed the peaks for three oxygen components in Cu/O-FLP catalyst, including C=O, C–O–C and C–OH [27–30]. After impregnating in alkaline solution, the C–O–C bond in Cu/O-FLP* sharply decreased from 37.96% to 23.19%, indicating that the epoxy in the C–O–C group were destroyed (Fig. 1a). The content of C–OH bond significantly increased and a clear peak appeared in the Na 1s spectrum (Fig. 1a and Fig. S1 in Supporting information), further confirming the epoxy in C–O–C group undergone ring cleavage and formed C–O–Na bonds [31]. This indicated that the C–O–C group was present as both epoxy and ether in the Cu/O-FLP catalyst, whereas in Cu/O-FLP*, it was solely existed as an ether bond. Fourier transform infrared spectroscopy (FT-IR) also showed a decrease in the intensity of the C–O–C peaks for Cu/O-FLP* catalyst (Fig. 1b) [30]. Furthermore, the Cu/O-FLP* catalyst showed a peak 530.1 eV which indicated the presence of the Cu–O bond [32,33]. This suggested that the Cu ions give rise to empty orbitals while OH$^-$ provide coordination electrons to form a covalent Cu–OH bond in alkaline solution (Fig. 1a). The Cu 2p spectra was shown in Fig. 1c, the main peak with a binding energy of about 934.7 eV ascribed to Cu^{2+}, and the peak with a binding energy of about 932.9 eV ascribed to Cu^{+} [34,35]. The peak positions of Cu in Cu/O-FLP and Cu/O-FLP* revealed that the Cu species appear at oxidation states instead of metallic states. And a slight peak shift to higher binding energy and a significant increase in the ratio of Cu^{2+} can be observed from Cu/O-FLP to Cu/O-FLP*, illustrating that the coordination electrons provided by –OH groups enhanced the electron-deficient state of Cu species [36]. Simultaneously, the N 1s and Cl 2p XPS spectrum presence of Cu–N [37] (Fig. S2 in Supporting information) and Cu–Cl [38] (Fig. S3 in Supporting information) bond in Cu/O-FLP and Cu/O-FLP* catalysts.

The chemical state and coordination environment of Cu species were further investigated by the extended X-ray absorption fine structure (EXAFS) spectroscopy measurements. Fig. 1d showed the Cu K-edge X-ray absorption near-edge structure (XANES) curves of the catalyst and reference samples. In the XANES spectra, the near-edge absorption energy of Cu/O-FLP [7] and Cu/O-FLP* were located between Cu foil and CuO, suggesting the Cu of catalysts existed in the form of oxidation state [39]. The oxidation state of Cu in the Cu/O-FLP* was increased, as evidenced by the shift of the XANES edge toward higher energy, which was consistent with the results of XPS [40]. In comparison with the Fourier transforms (FT) EXAFS (Fig. 1e) for Cu foil, the absence of a Cu–Cu scattering path ($\sim$2.19 Å) for the samples revealed that Cu species exist as isolated Cu atom [13,41,42]. Specifically, the major peak for Cu/O-FLP* splits into two shoulders at 1.07 and 1.53 Å and the intensity of the peak increased sharply, it means that there was significant variation in the local coordination structures. The wavelet transforms (WT) of the k^2-weighted EXAFS spectra in Fig. S4 (Supporting information) show the structure information in both k and R spaces. The WT contour plots of Cu/O-FLP* exhibited one intensity maximum at $\sim$4.4 Å^{-1}, which can be assigned to the backscattering of Cu–N or/and Cu–O bonds by comparing with CuPc ($\sim$4.5 Å^{-1}) and CuO ($\sim$4.3 Å^{-1}). In our previous article, the Cu/O-FLP [7] with a Cu-*cis*-N_2C_2Cl moiety (Cu coordinated with two N and two C atoms in the cis-configuration and an axial Cl atom), and the local coordination configurations of Cu/O-FLP* was further investigated by quantitative least-squares EXAFS fitting analyses. As depicted in Fig. 1f, the best-fit result for Cu/O-FLP* consisted of Cu–N/O and Cu–Cl, and the coordination numbers in the first coordination shell of Cu were estimated to be 5 and 1 (Table S1 and Fig. S5 in Supporting information), respectively. The coordination number of Cu in Cu/O-FLP* was 6 compared with that in Cu/O-FLP, which further indicated that the Cu atom formed coordination bond with –OH, consistent with the result of XPS. In brief, there results confirmed that the epoxy in C–O–C group at Cu/O-FLP* catalyst undergone ring cleavage after immersion in alkaline solution, while the coordination structure of Cu was adjusted to Cu-C_2N_2OCl moiety.

The catalytic performance of the prepared catalysts was conducted under the chosen operating condition (Fig. 2a), the Cu/O-FLP catalyst exhibited an acetylene conversion of approximately 61.4% and a relatively stability within 9 h. In comparison, the Cu/O-FLP* catalyst showed the initial conversion was 33.8% and the acetylene conversion decreased to 25.4% within the same condition. The VCM selectivity of Cu/O-FLP catalyst had reached more than 99%, but Cu/O-FLP* was only 95% (Fig. S6 in Supporting information). Meanwhile, the turnover frequency (TOF) value of Cu/O-FLP catalyst was 1.6-fold higher than that of alkaline treated catalyst (Fig. 2b). The loading amount of Cu atoms in the Cu/O-FLP and Cu/O-FLP* catalyst is 4.1 wt% and 3.9 wt% (Table S2 in Supporting information). The TOF was an important parameter for evaluating catalytic center, obviously, the content of Cu was not the major factor affecting the catalytic performance due to the alkaline treatment would not lead to the loss of copper. Although the Cu active sites in Cu/O-FLP* catalyst were more electron deficient compared with Cu/O-FLP, the catalytic performance may not be improved by excessive electron deficiency of Cu sites.

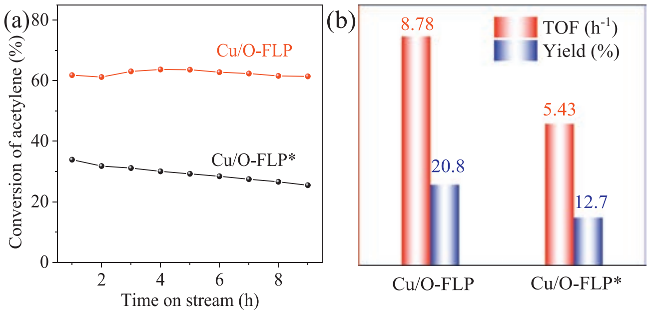

Fig. 2. Catalyst performance evaluation over Cu/O-FLP and Cu/O-FLP* catalyst. (a) The conversion of acetylene. Reaction conditions: 180 °C, $V_{HCl}/V_{C_2H_2} = 1.15$ and GHSV(C_2H_2) = 180 h^{-1}. (b) TOF value and vinyl chloride monomer yield.

Further considering the significant difference in initial activity between Cu/O-FLP and Cu/O-FLP*, combined with previous report suggesting that single-atom Cu and epoxide group could synergistically promoted adsorption and dissociation of HCl for acetylene hydrochlorination, we investigated the chemical state of the catalyst after activation with HCl. The Cl 2p XPS spectra (Fig. S7, Tables S3 and S4 in Supporting information) showed that the C–Cl species could be formed by the activation of HCl and the content of C–Cl species was similar to that of Cu/O-FLP-HCl and Cu/O-FLP*-HCl, which proved that the C–Cl species was not the main factor affecting the catalytic performance [43]. The high-resolution XPS spectra of O 1s for Cu/O-FLP and Cu/O-FLP-HCl (Fig. 3a) exhibit similar peak positions, which illustrated that the three oxygen components in the catalyst remain unchanged after activation of HCl. The content of C–O–C decreased significantly with the increase of C–OH content, which indicated that the presence of epoxide groups in C–O–C and the activation of HCl caused cleavage and protonation to form C–OH bond by ring opening reaction. It means that the epoxy group played a promoting role in H–Cl cleavage and accepts protons from HCl to obtain C–O–H bonds, the extra Cl atom of HCl interacted with Cu atom to form the Cu–Cl bonds. However, the content of C–O–C and C–OH groups in Cu/O-FLP* and Cu/O-FLP*-HCl (Fig. 3b) remain the same, due to the fact that the epoxy group on the catalyst had been ring opened when impregnated with alkali solution, resulting in the inability to assist in the dissociation of HCl at the Cu active site. Furthermore, the Cu–OH bonds formed by alkaline impregnation disappeared for Cu/O-FLP*-

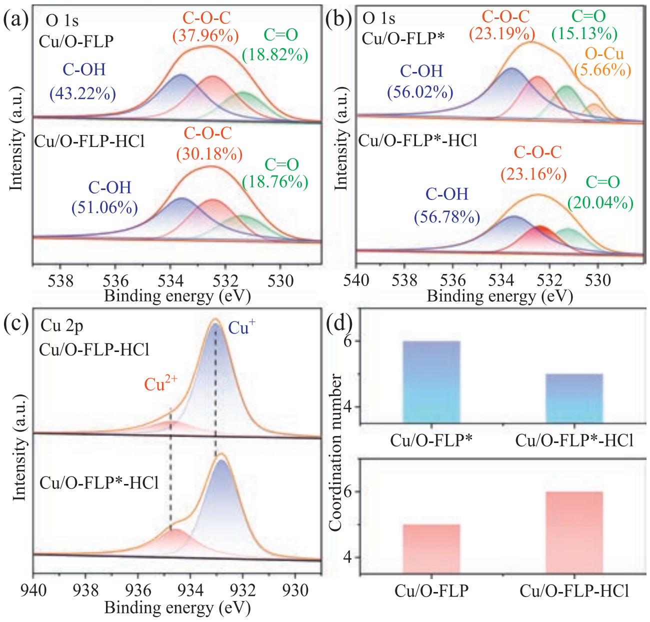

Fig. 3. The chemical state of Cu/O-FLP-HCl and Cu/O-FLP*-HCl catalyst. (a) The O 1s XPS spectra of Cu/O-FLP and Cu/O-FLP-HCl. (b) The O 1s XPS spectra of Cu/O-FLP* and Cu/O-FLP*-HCl. (c) The Cu 2p XPS spectra of Cu/O-FLP-HCl and Cu/O-FLP*-HCl. (d) Coordination number of Cu/O-FLP, Cu/O-FLP*, Cu/O-FLP-HCl and Cu/O-FLP*-HCl.

HCl, the Cu−OH coordination bond ruptured *via* the substitution reaction of hydrogen ions with hydroxyl groups on the Cu coordination bond. The Cu 2p spectra of catalysts (Fig. 3c) with HCl activation showed the proportion of Cu^{2+} in Cu/O-FLP*-HCl decreased compared with Cu/O-FLP*, which is similar to Cu/O-FLP-HCl further indicating that the Cu−OH coordination bond cleavage.

The chemical state and coordination environment of Cu species in Cu/O-FLP-HCl and Cu/O-FLP*-HCl were further investigated by the XAS measurements. As shown in Fig. 3d, Fig. S8 and Table S1 (Supporting information) the coordination numbers from Cu/O-FLP to Cu/O-FLP-HCl are estimated to be 5 and 6, which directly confirmed that the HCl was activated and the Cl atom binding with Cu atom to form the Cu−Cl bonds. This result implied that the activation and dissociation of H−Cl require the synergism of epoxy groups and Cu active sites. However, the coordination number of Cu/O-FLP* and Cu/O-FLP*-HCl were 6 and 5, respectively. The Cu sites in Cu/O-FLP* were a saturated coordination state, the hydroxyl coordinated with the Cu site was braked to forming a five-coordinated structure after HCl activation. Unlike Cu/O-FLP-HCl, the Cu atom in Cu/O-FLP*-HCl featured an unsaturated coordination site after HCl activation, but it does not form the extra Cu−Cl coordination bond with Cl atom. This was due to the opening of the epoxy group in C−O−C after Cu/O-FLP* was immersed in an alkaline solution, which resulted in the inability of the Cu sites to dissociate HCl synergistically with the epoxy group. This phenomenon not only induced the contact of Cu active sites with acetylene, but also verified the reason for the poor initial activity of Cu/O-FLP* catalyst in acetylene hydrochlorination reaction.

Reaction kinetics were implemented to probe the effect of the catalyst on the adsorption properties of the reactants. The activation energy (E_a) was obtained by experiments at different temperatures and Arrhenius equation fitting (Fig. 4a), and the E_a of Cu/O-FLP and Cu/O-FLP* were 24.4 and 29.3 kJ/mol, respectively. This result suggested that the synergistic coupling of Cu and adjacent epoxy sites could reduce the energy barriers of the reaction. In addition, the reaction orders of HCl and C_2H_2 were 0.44 and 0.32 for Cu/O-FLP (Fig. 4b), indicating that a more critical role for HCl in the reaction mechanism. For the Cu/O-FLP* (Fig. 4c), the reaction orders of C_2H_2 and HCl were 0.42 and 0.44, which revealed the competitive adsorption between C_2H_2 and HCl on the Cu site reduced the reaction rate. The slight difference between the two reaction orders indicated that the adsorption properties of Cu/O-FLP* catalyst have been altered, which was due to the absence of epoxy group adjacent to the Cu site to promote adsorption and cleavage of HCl. And the adsorption capacity of Cu/O-FLP and Cu/O-FLP* catalysts for HCl was carried out to further explore the influence of epoxy groups on the adsorption of reactants. As shown in Fig. 4d, it can be seen that the desorption peak of HCl at ~230 °C, and the desorption peak area of Cu/O-FLP was significantly larger than that of Cu/O-FLP*. The presence of epoxy groups in Cu/O-FLP led to greater adsorption capacity for HCl than Cu/O-FLP*. Meanwhile, the C_2H_2-TPD curve was shown in Fig. 4e, and slightly reduces the adsorption amount of C_2H_2 of Cu/O-FLP than that of Cu/O-FLP*. Comprehensively, the Cu/O-FLP can obviously enhance the adsorption of HCl, which was the reason for the improvement of catalyst activity.

In summary, to probe the mechanism of the effect of C−O−C groups on the Cu single atoms active site, the ring opening reaction of epoxy groups in the catalyst were performed using alkaline solution immersion. The performance of Cu/O-FLP in acetylene hydrochlorination was significantly better than Cu/O-FLP* without the epoxy group. The experimental characterizations confirmed that the synergistic coupling of Cu and epoxy sites could facilitated the adsorption and dissociation of HCl to form C−OH and Cu−Cl bonds to enhance the catalytic performance. And the ether in C−O−C group linked to the Cu site induced competitive adsorption of the reactants and increased the reaction energy barrier. This work provides some ideas for the design and optimization of oxygen functional groups on the carbon material in the future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

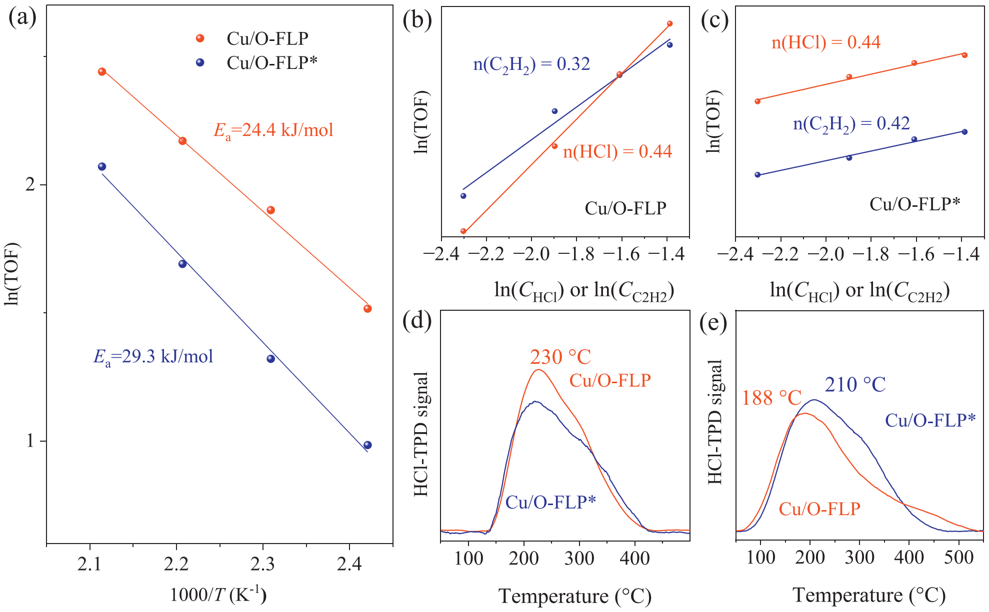

Fig. 4. The adsorption properties of substrates from kinetic reaction orders of Cu/O-FLP and Cu/O-FLP*. (a) Kinetic studies of Cu/O-FLP and Cu/O-FLP* catalyst. (b, c) HCl and C_2H_2 reaction order over Cu/-O-FLP and Cu/O-FLP*. Reaction conditions: $T_{bed} = 453$ K, $F_T = 20$ mL/min, C (C_2H_2, HCl) = 10–25 vol%, $W_{cat} = 0.1$ g, and P = 1 bar. (d) HCl-TPD profiles and (e) C_2H_2-TPD profiles of Cu/-O-FLP and Cu/O-FLP*.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.109508.

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