CO hydrogenation conversion driven by micro-environments of active sites over iron carbide catalysts

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Highlights

- The electronic properties and geometrical effects have an integrated effect on CO activation behavior, for the former can distinguish the CO activation routes and the latter greatly affects the energy barriers of CO activation.
- The defective sites were not the only sites to dissociate CO, as CO always tended to dissociate in a wider area.
- The electronic properties could effectively describe the C-C coupling process, as well as distinguish coupling mechanisms.

1. Introduction

Essentially clearing the structure–activity relationship between iron carbide catalysts involving multiple active centers to understand the reaction mechanism of CO hydrogenation conversion process is still a great challenge. Combined with the effective calculation of spin-polarized density functional theory (DFT), studies have reported on the process descriptors of CO hydrogenation conversion from multiple perspectives [1-3], which rely on two factors, namely electronic properties and the local environment. Currently reported process descriptors have focused on a single crystal phase, while in the actual reaction process, the iron carbide catalyst serves as a combination of multiple crystal phases. In this study, we presented theoretical investigations focusing on the regulation of micro-environments involving multiple active sites, with the goal of deeply analyzing and understanding the reaction mechanism and structure–activity relationship of the CO hydrogenation process over iron carbide catalysts.

2. Methods

All DFT calculations were carried out by the Vienna ab initio simulation package (VASP) with Perdew-Burke-Ernzerh of (PBE) exchange-correlation functional and projector-augmented wave (PAW) pseudopotential. The spin polarization was included due to the magnetism of iron carbides, and the frequency analysis was also included for all monomers and adsorbed states to avoid the imaginary frequencies for all degrees of freedom.

3. Results and discussion

A correlation between the Bader charges of the surface Fe atoms and CO activation barriers was established, as shown in Figure 1a, revealing a direct effect on the CO activation behavior. Lower Bader charges were accessible for direct CO activation (yellow zone), and H-assisted CO activation was favorable in higher Bader charges (blue zone). Therefore, the electronic property played a crucial role in distinguishing these two CO activation mechanisms. The concept of N_{Fe}/nm^2 was adopted to study the relationship between the spatial configuration and CO activation behaviors. By correlating the number of active Fe atoms per supercell area (N_{Fe}/nm^2) with their charge values, we observed that the Bader charge of the active metals was related to the spatial configuration of the active sites (Figure 1b). The spatial configuration of the active sites significantly affected the energy barrier level of CO activation. Notably, the differences in spatial configurations divided the energy barriers of CO dissociation on multiple crystal planes into four regions (Figure 1c). Clearly, the narrower the spatial configuration of the active sites, the higher the energy barriers of CO activation, and the wider the spatial configuration of the active sites, making it easier to break the C-O bonds. Therefore, for the catalytic process involving the dynamic changes in the active sites, a geometrical effect of local micro-environments based on the electronic effect was observed. So constructing defect sites has served as an

effective strategy for reducing the energy barriers of CO activation. Interestingly, we observed that the defective sites were not equivalent to the active sites of CO dissociation, and if the spatial configurations of the defective sites were not wide enough, CO would still dissociate at the original sites.



Figure 1. (a) Relationship between the energy barriers of CO activation (Ea) and the Bader charges (qB) of the surface Fe atoms involved in CO dissociation. Diagram showing the number of Fe atoms per unit area (N_{Fe}/nm²) with the Bader charge (qB) (b) and the energy barriers of CO activation (E_a) (c) on iron carbide catalysts. (d) Relationship between E_{eff,C1+C1} with the Bader charges (qB) of the involved surface Fe atoms of the active sites on different iron carbide catalyst surfaces.

To understand the structure–activity relationships in the environment-dependent reaction, the Bader charges (q_B) of the surface Fe atoms on the active sites were examined in relation to the energy barriers of C-C coupling process. For the C-C coupling process, a good linear correlation between $E_{eff,C1+C1}$ and q_B was observed, as shown in Figure 1d. This indicated that the electronic property was a good descriptor for C-C coupling, where the lower the q_B , the stronger the electron-transfer ability of the surface Fe atoms, and the easier the formation of the C-C coupling products, and vice versa. Notably, this descriptor could distinguish two different coupling mechanisms, where one consisted of the coupling of surface carbons and the other was the coupling of dissociative carbons.

4. Conclusions

Two main structural factors, namely the electronic properties and the geometrical effects, were found to have an integrated effect on the mechanism of CO hydrogenation conversion over iron carbide catalysts mixed with multiple active phases. The charge transfer of the surface metals on the active sites had a guiding effect on the CO activation pathway. Further, the spatial configuration of the active sites greatly affected the energy barriers of CO activation, where the wider the spatial configuration of the active sites, the lower the energy barriers of CO activation. Notably, the defective sites were not the only sites to dissociate CO on the defective surfaces, as CO always tended to dissociate in a wider area. Also the electronic properties could effectively describe the C-C coupling process, as well as distinguish coupling mechanisms.

References

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Keywords

Micro-environment, CO hydrogenation conversion, electronic property, local environment