

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 $N_{\text{Fe}}/\text{nm}^2$ 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 ($N_{\text{Fe}}/\text{nm}^2$) 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

