Theoretical studies on the “electron reservoir” effects of supported vanadia/ceria catalysts

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Abstract:

Ceria-supported vanadium oxides have been found to be extremely active in selective oxidative dehydrogenation (ODH) reactions. In this work, we systematically studied the structures and especially the origin for the unique activity of VO_x/CeO_2. We found that the activity of VO_x/CeO_2 is closely related to the hydrogen adsorption energy, which is largely controlled by the electronic effect. Specifically, some monomeric VO_x species can modify the electronic structure of the supporting ceria. The structural effect was found to be able to influence the activity as well. These results may help us to understand the unique catalytic activity of vanadia/ceria.

Keywords: Twinning Boundaries, Evolutionary Algorithm, Reactive Force Field.

1. Introduction

Most heterogeneous catalysts take the form with active species as clusters supported at inert or active metal oxide supports. As a particular example, catalysts based on supported vanadium oxide exhibit remarkable activity for selective oxidative dehydrogenation (ODH) reactions.[1-3] As compared with irreducible oxides, like silica or alumina, ceria supported vanadia (vanadia/ceria) has been found to be particularly active.[1-3] However, the underlying mechanisms for the ultrahigh catalytic activities of vanadia/ceria catalyzed ODH reactions have not been well understood yet. More importantly, the studies of vanadia/ceria, as a model catalyst, failed to provide any deep understanding into the general roles of electronic and structural properties of the system in catalytic reactions.

2. Computational details

The PBE functional with the dispersion correction of DFT-D scheme was employed to do the spin-polarized calculations by using the Vienna ab initio Simulation Package (VASP)[4]. The DFT+U approach with a Hubbard U of 5.0 eV was applied to describe the localized Ce 4*f* states. The electron-core interaction was described by using the project-augmented wave (PAW) method at a kinetic energy cutoff of 400 eV. The monomeric vanadia clusters were deposited on the $CeO_2(111)$ support which was extended at a (4×4) surface cell. The slab model contains a large vacuum gap (>10 Å) and nine atomic layers with the bottom three layers being fixed in all calculations to estimate bulk properties.

3. Results and discussion

The thermodynamic stabilities of large variety of VO_x (x=2-4) species have been thoroughly compared and their involvement in catalytic reactions have also been calculated. It is interesting to find that for supported VO_4, the thermodynamically most stable one is actually less important than a metastable one, which is the actual catalytic species in the reaction cycle. Calculations of the catalytic performance of different oxygen species in oxidation of methanol to formaldehyde suggested that the H adsorption strength at these O species can be a good descriptor of their ODH activities (Figure 1a). Moreover, oxygen of the interface V-O-Ce group are catalytically more active, especially when H adsorption energy is small, indicating the strong structural effect in the vanadia/ceria supported catalyst (Figure 1a). More interestingly, we determined the new empty localized states (NELS) of O 2*p* generated in ceria-supported system through depositing VO_3- and VO_4-type monomeric vanadia species (Figure 1b). Such NELS are found to participate in the whole ODH reaction processes and help to reduce the barriers at various steps, reflecting the unique role of the NELS in attuning the activities of surface oxygen species (Figure 1c).

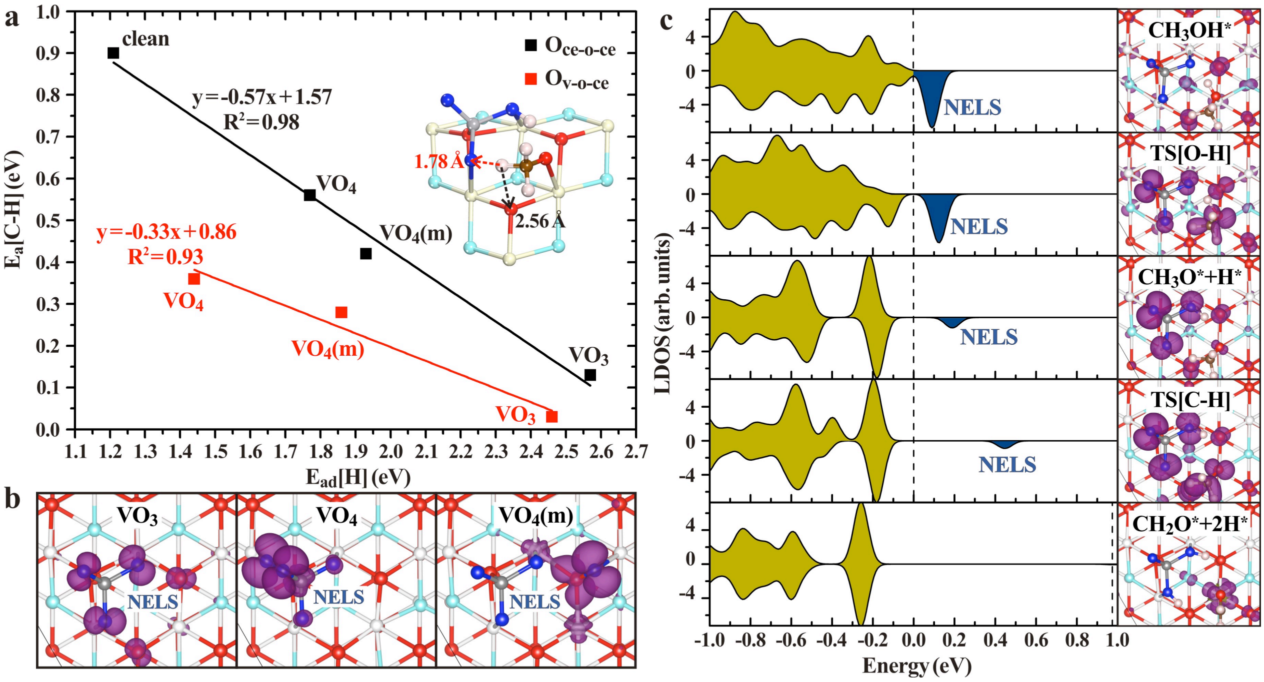

Figure 1. (a) Correlations for H adsorption energy and the barrier of rate-limiting C-H breaking step through $O_{ce\text{-}o\text{-}ce}$ or $O_{v\text{-}o\text{-}ce}$ route. Inset: C-H bond breaking scheme (at VO_3). Ce atoms are in ivory, V in grey, C in brown, H in pink and O above the $CeO_2(111)$ surface in deep blue. O atoms of top- and sub-surface are in red and cyan, respectively. (b) Lowest unoccupied molecular orbitals (LUMO) distributions of VO_3, VO_4 and VO_4(m). Isosurface (purple) levels were set at 0.004 $Å^{-3}$. (c) Calculated local density of states (LDOS) and highest occupied molecular orbital (HOMO) distributions for the states along H abstraction ($CH_3OH^* \rightarrow CH_3O^* + H^* \rightarrow CH_2O^* + 2H^*$) through $O_{v\text{-}o\text{-}ce}$ route at VO_3.

4. Conclusions

In summary, we performed DFT calculations to illustrate the underlying mechanisms. It is found that unique electronic and structural effects are both crucial in the catalytic processes. Calculations of the catalytic performance of different oxygen species in oxidation of methanol to formaldehyde suggested that the oxygen of the interface V-O-Ce group are catalytically more active, especially when H adsorption energy is small, indicating the strong structural effect in the vanadia/ceria supported catalyst. In addition, NELS of O 2*p* generated in ceria-supported system through depositing VO_3- and VO_4-type monomeric vanadia species are determined to participate in the whole ODH reaction processes and help to reduce the barriers at various steps. We believe that the proposed electronic and structural effects are crucial to understanding the mechanisms of ODH reactions on vanadia/ceria and many other catalytic systems, and they may also help design new catalysts.[5]

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