



Editor's choice paper

Insights into the metal-support interaction between NiCu cluster and MgO as well as its effect on H adsorption and H₂ dissociation



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ABSTRACT

Density-functional theory has been conducted to investigate the interactions of bimetal NiCu with MgO at the atomic and electronic level as well as its effects of H adsorption and H₂ dissociation, compared with those on Ni/MgO. Two models including Ni₂Cu₂ cluster supported on perfect MgO(001) and oxygen-vacancy MgO(001) are built to represent bimetal NiCu anchored on MgO catalysts. The results show that there is stronger metal-support interaction in Ni₂Cu₂/MgO catalyst with oxygen-vacancy than that in perfect Ni₂Cu₂/MgO catalyst, and the H adsorption on defective Ni₂Cu₂/MgO is stronger than that on perfect Ni₂Cu₂/MgO. Correspondingly, H₂ dissociation is faster on defective Ni₂Cu₂/MgO than that on perfect Ni₂Cu₂/MgO. Compared with Ni₄/MgO, the interaction between metal and support is weaker on the corresponding Ni₂Cu₂/MgO, and the interaction of H and substrate is stronger, moreover, the H₂ dissociation is faster on defective Ni₂Cu₂/MgO while it is not changed on perfect Ni₂Cu₂/MgO. The results indicate that the addition of Cu to defective Ni/MgO can improve the dissociation of H₂, which provides a clue for tuning catalyst performance by modifying the metal-support interaction.

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1. Introduction

In recent years, metal-support interaction has been considered as a fairly important part of heterogeneous catalysis due to its influence on catalytic performance. In general, the interaction exists in transition metal supported on oxide support surface [1–5], such as MgO, Al₂O₃ and SiO₂. The metal-support interaction is mainly presented by special morphology and charge transfer between metal active component, and support is deemed to have very significant effect. The charge-modifying effect of the support makes the metal particles on the surface of the support change greatly, inducing the unique catalytic activity [6–9]. Ratkovic et al. [10] reported that different degrees of weak metal-support interaction exhibit in Fe-(Ni)/Al₂O₃ catalyst, which govern activity and selectivity in producing carbon nanotubes using ethylene. Ewbank et al. [11] used two methods (controlled adsorption and dry impregnation) to pre-

pare the Ni-based catalysts being of different catalytic effect, which differs primarily in metal-support interactions.

H and H₂ are often used as probe molecule to examine the catalyst performance. Importantly, H adsorption and H₂ dissociation or formation are widely involved in the reactions catalyzed by Ni-based catalysts, such as CO methanation, CO₂ methanation, CH₄/CO₂ reforming, CH₄/H₂O reforming [12–17]. Supported Ni catalysts are high activity for the above reactions. However, carbon deposition seriously prevents its industrialization. In order to remove the disadvantage, some methods, such as addition of a second metal and modifying the support are tried to tune the interaction between metal and support interaction, further to change the catalyst performance. It was reported that Cu addition to Ni/Al₂O₃ catalyst has superior performance to suppress the carbon deposition during CO₂ reforming of methane [18–20]. The bimetal catalyst is of good catalytic performance, not only because of the synergy effect between Ni and a second metal, but also metal-support interaction. The results show that the reactivity of catalyst is sensitive to morphology and dependent to degree of synergetic effect between Ni and Cu particles. Meanwhile, it is feasible to synthesize the composites of NiCu alloy particles fixed in MgO. Chesnokov et al. [21] used high-resolution electron microscopy

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to study the Ni-Cu/MgO catalyzed 1,3-butadiene decomposition. The NiCu/MgO catalysts also have been prepared using the fusing method [22] and incipient wetness impregnation [23]. The metal-support interaction can be evaluated by density functional theory method at the atomic and electronic level. For example, Delbecq et al. [24] reported the metal-support interaction on the chemical reactivity for the hydrogenation of crotonaldehyde by Pt₁₃ clusters deposited on CeO₂(111) model system. DFT has been applied for elucidating the atom and electron transfer between metal particles and oxide supports, detailed structure of interface, and hydrogenation mechanism [25–28]. Wang et al. [29] calculated the binding energies of 19.0, 25.2, 46.7 and 17.3 kcal/mol for metal (metal = Ni, Pd, Pt or Cu) on perfect MgO(100) surface and of 25.8, 59.7, 85.2 and 19.1 kcal/mol on the MgO(100) surface with an oxygen vacancy. Atomic adsorption of 11 non-metals (H, B, C, N, O, F, Si, P, S, Cl, and Br) on defect-free MgO(001) surface has been investigated [30]. The calculated adsorption energies range from –0.56 eV (hydrogen adsorption) to –2.63 eV (carbon adsorption). In the same kind of supported catalyst, is it good for the reaction to strong or weak interaction between metal and support? Cui et al. [31] considered that moderate metal-support interaction is necessary to ensure the high activity and stability of the Ni/Al₂O₃ catalyst for syngas methanation. Zhao et al. [32] reported that strong metal-support interaction leads to superior activity of Ni/SiO₂.

The non-polar (001) surface of magnesium oxide is one of the most studied theoretically [33–35]. Its relatively simple structure does not bear significant relaxation or reconstruction and supplies for a good model for expressing adsorption features of small probe molecules or deposited transition metal atoms. In this respect, point defects or morphological irregularities on the oxide surface can affect the chemical properties of the particle, hence its catalytic activity. The isolated metal atoms which are inert when deposited on the regular MgO(001) sites develop a specific activity when bound to surface defects [36,37]. In MgO, oxygen vacancies result in the formation of a surface cavity with one or two trapped electrons, giving rise to the classical F centers of ionic crystals [38,39]. F_s centers at a MgO surface are one kind of point defects where diffusion of atoms can be inhibited [40]. In addition, a neutral F vacancy is formed when an oxygen atom is removed from the surface.

For MgO supported Ni-based bimetal catalysts, there is only a little work focused on the tuning the interaction of metal-support, further changing the catalyst performance. The detailed contribution about the active component and MgO structures, the electron transfer between metal and MgO as well as the metal-support effect on the reaction, is scarce. A basis understanding and optimization of the metal-support interaction is scientifically and technologically significant for rational design of high performance catalysts [41]. Previous studies have suggested that the supported CuNi bimetallic catalysts with an approximate ratio of Ni/Cu to one have beneficial effects on the catalytic performance [42,43]. Gate et al. [44] reviewed synthesis, structural characterization, and catalysis by supported bimetallic clusters and prepared the supported Ir₄ catalyst samples by decarbonylation of [Ir₄(CO)₁₂] on porous γ -Al₂O₃ or of [H₂Ir₄(CO)₁₁] on MgO [45,46]. Meanwhile, this tetrahedral configuration cluster of four atoms is the smallest and most stable configuration which can provide a three-dimensional structure to probe both metal-metal and metal-support interactions as reported in many other studies [47–49].

DFT studies can provide information about the electronic structure of the surface metal atoms and the adsorbate atoms through atom-projected densities of states (PDOS). PDOS has been proven useful for studying the interaction of substrate and adsorbate through the effect they have on the electronic structures of the substrate metal atoms. The basic idea to study PDOS is that trends in the interaction energy between adsorbate and metal surface are governed by the coupling *sp* states from adsorbate to *d*-bands from

metal, since the coupling to *sp* states of metal is essentially the same. Consequently, the coupling between the adsorbate and the substrate is included in two steps. First, the adsorbate is coupled to *sp* states from metal, which leads to a shift and broadening of the adsorbate states. The renormalized adsorbate states are then coupled to *d*-states from metal. If the inclusion of the coupling to the *d*-states is a small perturbation of the system then this contribution to the total energy can be calculated simply from the change of the sum of the (Kohn–Sham) one-electron energies. If the coupling to the metal *sp* states can be considered to be similar for a group of surfaces, trends in adsorption energies will depend primarily on the coupling to the metal *d*-states, which then depends primarily on the factors listed above. Other factors like the width and shape of the *d*-band also influence the coupling energy, but these are generally smaller corrections [50]. In the present work, we explored DFT calculations with periodic slab model to investigate the interactions between bimetals Ni₂Cu₂ and MgO surfaces as well as their effects on H adsorption and H₂ dissociation, and compared those on Ni₄/MgO.

2. Computational details

2.1. Computational model

Based on the model of Ni₄/MgO, we selected two Cu atoms replace two Ni atoms in Ni₄/MgO(001) as the model of NiCu(Ni:Cu = 1:1) bimetal supported on perfect MgO. The lattice constant of MgO(001) is optimized to be 4.301 Å, which is consistent with the experimental value, 4.213 Å [51]. A four-layer MgO(001) slab is used Ni₂Cu₂/MgO catalysts, in which the bottom two layers are fixed in bulk position [52]. A (2 × 2) supercell was used in the calculation in order to reduce interaction between adsorbates on the surface. In order to explore the effect of the defective MgO(001) surface on the reaction mechanism, the defective Ni₂Cu₂/MgO model catalysts were established by removing a neutral oxygen atom linked with the Ni (or Cu) from the surface of MgO based on the most stable model of perfect Ni₂Cu₂/MgO.

The calculations being periodic in three dimensions, a vacuum of 12 Å was imposed between two consecutive slabs in order to eliminate any noticeable interaction with the periodic image along the *z* direction. During geometry optimization, the bottom two layers were fixed in their bulk positions, whereas the remaining two layers together with Ni₂Cu₂ and the adsorbed species were allowed to relax in all calculations.

2.2. Computational methods

All the calculations were performed in the framework of the density functional theory (DFT) by using the Cambridge Sequential Total Energy Package (CASTEP) [53,54] in Material Studio 5.5 of Accelry Inc. The generalized gradient approximation (GGA) had been chosen to represent the exchange–correlation potential in the formulation of the Perdew–Burke–Ernzerhof (PBE) [55,56]. In this framework, a large convergence of the plane wave expansion was obtained with an energy cut off of 340 eV. For geometry optimization, the Brillouin zone was sampled in a 2 × 2 × 1 Monkhorst–Pack set [57,58]. The geometries were not optimized, until the energy, the force and the max displacement converged to 2.0 × 10^{–5} eV/atom, 0.05 eV/Å and 2 × 10^{–3} Å, respectively. Spin polarization was considered throughout all calculations. Transition states (TS) were located by using complete linear synchronous transit (LST) or quadratic synchronous transit (QST) methods [59]. Firstly, LST maximization was performed by an energy minimization in the directions conjugated to reaction pathway. Then, the TS approximation was used to perform QST maximization. From that

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