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Full Length Article

The mechanism of the high resistance to sulfur poisoning of the rhenium doped nickel/yttria-stabilized zirconia

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ABSTRACT

The structural stability of the Ni_4 and $Ni_{4-x}Re_x$ clusters on the yttria-stabilised zirconia (YSZ) surfaces under sulfur adsorption is systematically studied using a first-principles method based on density functional theory. It is found that the $Ni_{4-x}Re_x$ alloy cluster is more difficult to deform under sulfur adsorption than the pure Ni_4 cluster on the YSZ(1 1 1) surfaces. The results are helpful for explaining why Ni alloyed with Re is more tolerant for sulfur poisoning and provide guidance for designing Ni-based catalyst with high sulfur tolerance.

1. Introduction

Solid oxide fuel cells (SOFC) that can convert chemical energy into electrical energy consist of three main elements: the cathode, the electrolyte and the anode. The conventional anode material of SOFC is the Ni/YSZ (yttria-stabilized zirconia) cermet, containing Ni nanoparticles [1]. In the Ni/YSZ anode, the Ni and YSZ provide electronic and oxygen-ion conduction, respectively. However, sulfur poisoning is a problem of the Ni/YSZ anode [2]. The fuel always contains ppm level of H_2S, which can easily dissociate on the Ni surfaces resulting in S atoms adsorbed on the surfaces [3]. As a result, the catalytically active sites will be blocked and the metal surfaces would experience reconstructions [4] after S atom adsorption, even with the formation of Ni-S compounds (Ni_3S_2, Ni_7S_6, and NiS) [2]. Many approaches have been developed to fabricate alloy materials to improve the sulfur tolerance of Ni-based catalysts for reforming reactions [5]. For example, Wang et al. [6] proposed that the Ni-Re/Al_2O_3 sample has outstanding performance maintaining hydrocarbon conversions activity in a sulfur containing stream at 580 °C temperatures. They also reported a similar positive effect with the addition of Re in a Ni/zeolite ZSM_5 system in a sulfur containing stream [7]. Murata et al. [8] found that among the Re, La, Nd, Sm, Ce, Yb, Eu, and Mo dopants, only La and especially Re enhanced sulfur tolerance of Ni-Sr/ZrO_2. It can be concluded that rhenium seems to be a very promising metal to diminish Ni sulfur poisoning, although the exact mechanism is still unclear. In order to study the metal/YSZ or ZrO_2 interaction, a number of researches have been carried out, e.g., the studies about the Ni_4 cluster on the t-ZrO_2(1 1 1) [9] or c-ZrO_2(1 1 1) [10,11] surfaces, or Pt_4 cluster on ZrO_2 surfaces [12] and CO_2 reforming on a Pt_4/ZrO_2(1 0 1) surface [13], as well as Ni atoms deposition on the YSZ(1 1 1) surfaces [14]. The interaction properties of sulfur with nickel or nickel rhenium alloy clusters on the YSZ surfaces are very important for understanding the mechanism of the high resistance to sulfur poisoning of the rhenium doped nickel/yttria-stabilized zirconia. In this work, we performed a systematic study on how the sulfur atom attacks the Ni catalysts on the YSZ(1 1 1) surfaces and how the Ni catalysts alloyed with Re can improve the stability of Ni catalysts under S atom attack. We found that the pure Ni_4 cluster on the YSZ(1 1 1) surface is very easily to be deformed under sulfur adsorption. In contrast, the $NiRe_3$ alloy cluster on the YSZ(1 1 1) surfaces is more difficult to deform under sulfur adsorption. The results are helpful for explaining why Ni alloyed with Re [6,7] was experimentally found to have resistance to sulfur poisoning and provide a clue for designing Ni alloy catalyst with high sulfur tolerance.

2. Model and computational method

We used the Vienna ab initio simulation package (VASP) to perform calculations which adopted the spin-polarized periodic density functional theory (DFT) method [15]. The exchange

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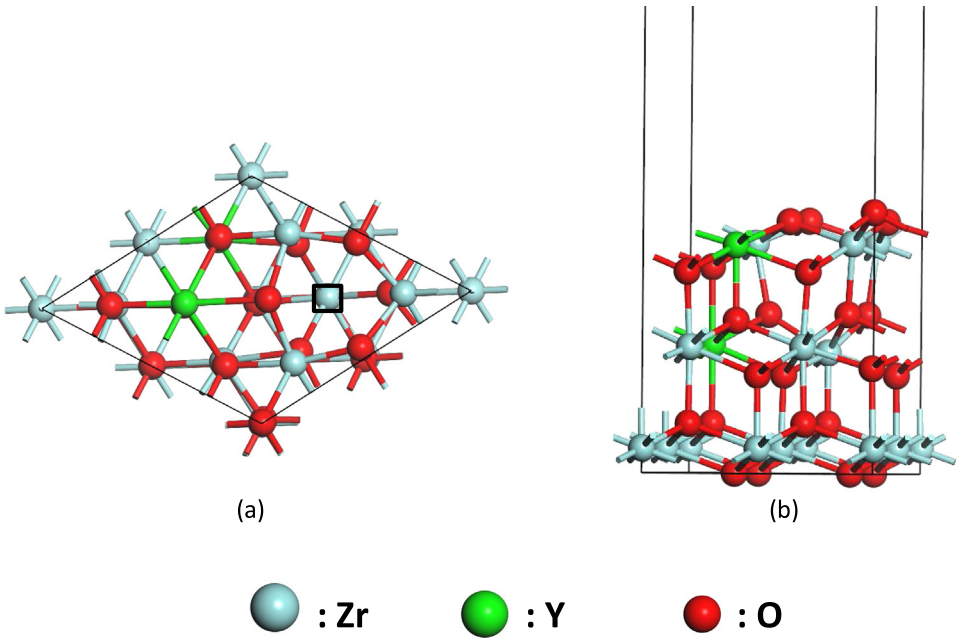

Fig. 1. The top (a) and side (b) views of YSZ(1 1 1) surfaces. The black square represents the intrinsic oxygen vacancy. The sky blue, green and red balls represent Zr, Y and O atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

correlation functional with generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [16] combined with the projector-augmented wave (PAW) [17] method was used to solve the Kohn–Sham equations. The O (2s 2p), Ni (3p 3d 4s), and S (3s 3p), Re (5d 6s), Zr(4d 5s), Y(4s 4p 4d 5s) electrons were treated explicitly as valence states and expanded in plane-waves

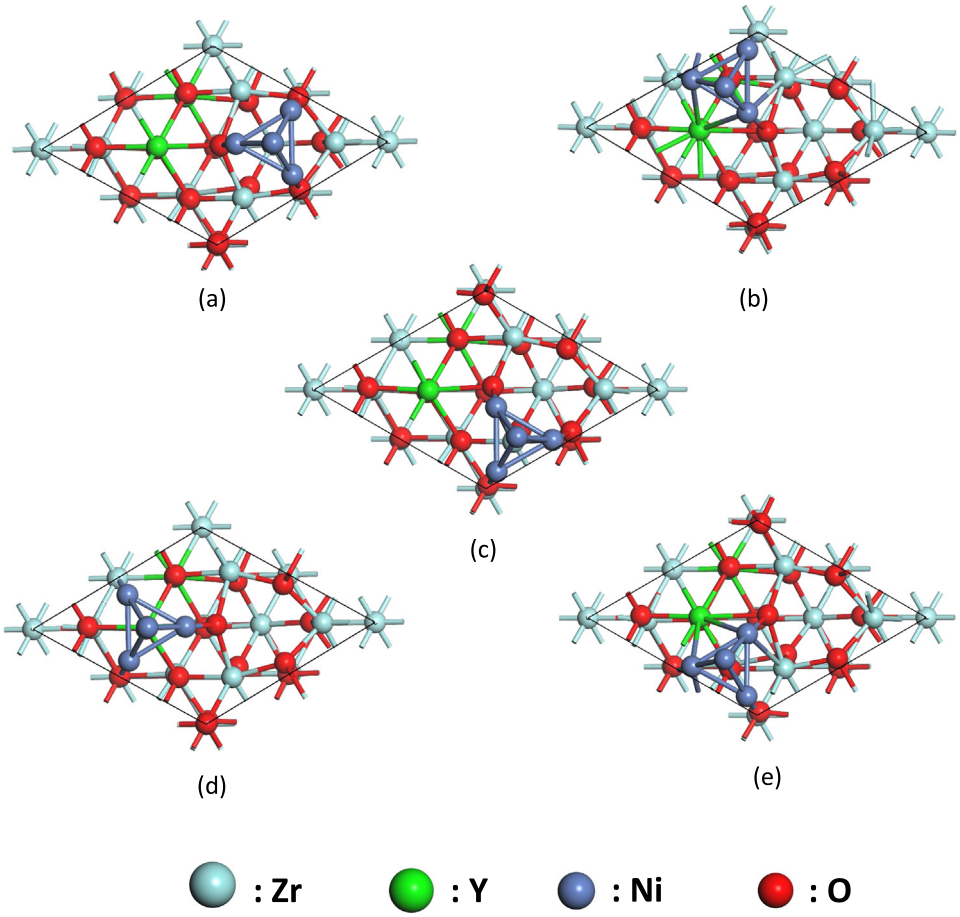

Fig. 2. The five optimized Ni_4 clusters adsorbed on the YSZ(1 1 1) surfaces. The sky blue, green, dark blue and red balls represent Zr, Y, Ni, O atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)