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Interfacial stability, electronic property, and surface reactivity of α-MoO_3/γ-Al_2O_3 composites: DFT and DFT + U calculations

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ABSTRACT

The design of α-MoO_3/γ-Al_2O_3 composite is of high interest because such composites are with extraordinary catalytic selectivity for petroleum refining. However, the role of each component in heterogeneous catalyst as well as the essential relationship between interfacial structure and surface reactivity is still ambiguous. To deeply understand these details, we investigated the structure, stability, electronic property, and surface reactivity of α-MoO_3/γ-Al_2O_3 composites by density functional theory DFT and DFT + U. The models of α-MoO_3/γ-Al_2O_3 composites were constructed by combining the α-MoO_3 (0 1 0) surface with non-spinel and spinel γ-Al_2O_3 (1 0 0) and (1 1 0) facets. We found that both the nature of γ-Al_2O_3 support and the surface coverage of α-MoO_3 significantly influenced the interfacial stability and surface catalytic activity. For all composites, the interfaces were stabilized *via* the formation of different Al—O—Mo bonds between the γ-Al_2O_3 slab and the α-MoO_3 slab. The interaction energy and adhesion work of interface indicated that the spinel γ-Al_2O_3 (1 1 0) surface is most favorable for the stabilization of α-MoO_3 surface. Fermi softness (S_F), a readily obtainable electronic property was used to evaluate the surface reactivity of the composites. The results indicated that the surface reactivity of all composites is clearly higher than pure α-MoO_3, and the monolayer coverage composites with exposed (1 1 0) surface of γ-Al_2O_3 exhibited the highest surface reactivity. By analysis of the charge density difference and density of states, we found that the electrons on the interface are largely redistributed and charges transfer from γ-Al_2O_3 to α-MoO_3, which promoted the delocalization of both interfacial and surface electronic states near the Fermi level, resulting in strengthened the interfacial interaction and surface reactivity. In addition, the adsorption and dissociation of H_2S on the surfaces of all ML composites was investigated. The reaction pathway and kinetic barrier were determined. The results shown that ML- Mo/nspAl(1 1 0) with the highest Femi softness (1.39) showed the lowest energy barrier (0.35 eV), which further confirmed the effectiveness of the Femi softness.

1. Introduction

In the past decade, Molybdenum trioxide (α-MoO_3) has been recognized as one of the most pivotal catalysts with high selectivity in petroleum industry and has been used in olefin metathesis [1], hydrogen/oxidative desulfurization [2–4], selective oxidation [5–7], hydrodeoxygenation [8–10], etc. As interests in MoO_3 related field are steadily growing, several intriguing applications in supercapacitors [11,12], optics [13–15], and gas sensors [16,17] were also reported. However, α-MoO_3 particles with high concentration are easily agglomerated by high surface energy and quickly lose the catalytic activity under harsh reaction conditions [18–22]. Hence, a series of oxide supports, *e.g.* γ-Al_2O_3, SiO_2, TiO_2, ZrO_2, and CeO_2 is usually introduced to improve the catalytic activity of α-MoO_3. Among them, γ-Al_2O_3 is one of the most widely used supports due to good mechanical strength, excellent thermal stability, large surface area, and low cost [23,24]. The highly dispersed molybdena on alumina support showed pronounced catalytic activity in numerous reactions [18,22,25].

It is well known that alumina support plays an important role in improving the activity of the molybdena catalysts. The strong catalyst-support interactions considerably influenced the geometric configuration, electronic properties, stability and growth of molybdena active

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phase and affected the catalytic reactions. Hence, the design of highly active catalysts demands a more complete understanding the characteristics of catalyst–support interface, which is the key for clarifying the essential influence of various preparation methods on the existing states of Mo species and their evolution in catalytic reactions. However, the catalysts-support interface is often complex for these heterogeneous catalysts. There is relatively limited knowledge about the relationship between interfacial structures and surface reactivity at the atomic and electronic levels. Some literature reported that the catalytic reactivity of molybdena/alumina catalysts can be attributed to the high dispersion of MoO_x species on γ-Al_2O_3 support [19–21,26–32]. Raman, UV–vis, EXAFS, NEXAFS and IR were used to identify the molecular structure of molybdena/alumina catalysts. When the Mo loading lower than monolayer coverage, both isolated dioxo and oligomeric mono-oxo Mo species coexist on the alumina support to form tetrahedral or octahedral coordinated structures. The capacity of the γ-Al_2O_3 support for the dispersion of molybdenum oxide is underutilized and the exposed γ-Al_2O_3 surface may have a negative impact on the catalytic activity. While at high Mo loading above monolayer surface coverage, the Mo has been fully dispersed on the support and crystalline MoO_3 nanoparticles are formed, which is not active to some catalytic reactions since the excess of MoO_x species cannot anchor to the support. Hence, the best catalytic performance is often observed when the surface of alumina is just covered by filled monolayer molybdena species with 3.4–5.9 Mo atoms nm^{-2} [33,34]. Periodic density functional theory (DFT) calculations of MoO_x sites on alumina also suggested that both monomeric and dimeric MoO_x clusters could be stabilized on alumina surface, and their relative stability depended on the exposed alumina (1 1 0) or (1 0 0) surface [35,36]. Although the location of the MoO_x active site on the alumina surface largely influences the reactivity, only a handful of detailed interfacial characterization data is available due to the limited number of MoO_x clusters located on the surface of alumina [19,20]. Furthermore, it is difficult to explore the interfacial effects on the surface reactivity at monolayer coverage or higher coverage by using the MoO_x cluster models, because the geometries of oligomeric mono-oxo Mo species on the γ-Al_2O_3 surface are more complex and varied. Consequently, the α-MoO_3 (0 1 0) surface might serve as the monolayer active Mo species since the natural layered structures of α-MoO_3 can be observed along (0 1 0) orientation and it is the lowest energy surface [37]. In fact, the two-dimensional α-MoO_3 (0 1 0) surface is often used as models to provide significant theoretical insights into the mechanism of certain catalytic reactions, *viz* ethylene hydrogenation [38], acetaldehyde hydrodeoxygenation [39], and chemisorption of allyl [40]. Nevertheless, the neglect of γ-Al_2O_3 [10,41] support may result in the misunderstandings of exact catalytic reactions. This is because the interfacial interaction leads to the complexity and the diversity of surface, which largely hindered the study of reaction mechanisms and kinetics.

Additionally, to experimentally and theoretically characterize the reactivity of MoO_3, probe molecules (e.g. hydrogen, ethylene, and methanol) were employed in the previously described reports. However, the use of these molecules means an unavoidable external perturbation. Hence, it is necessary to quantitatively describe the surface reactivity of catalysts using a more convenient and direct approach that does not introduce any disturbances into the system. Fukui functions were employed and proved to be valid as indicators of chemical reactivity for many systems [42,43]. Unfortunately, some researchers also found that Fukui functions are not always a suitable method to predict the reactivity of solid catalysts [44]. More recently, a new concept, the Fermi softness [45] has been proposed for the facially and quantitatively describes the surface activity of heterogeneous catalysts under finite temperatures. Despite the Fermi softness has been successfully utilized to compare the catalytic activity of various heterogeneous catalysts. However, to the best of our knowledge, there are few theoretical studies about heterogeneous α-MoO_3/γ-Al_2O_3 catalyst. Hence, it is necessary to probe the chemical reactivity of solid surface when the layered α-MoO_3 coated on the γ-Al_2O_3 support.

Table 1
Mismatch parameter (α) for γ-Al_2O_3 (1 1 0) and (1 0 0) surfaces in combination with the α-MoO_3 (0 1 0) surface.

γ-Al_2O_3 surfaces		Ratio of surface (%)	Surface energy (mJ m^{-2})	α (%)
Nonspinel	(1 1 0)	70–83 [53,54]	970 [49]	1.08
	(1 0 0)	17–30 [53,54]	1540 [49]	2.96
Spinel	(1 1 0)	70 [55]	1050 [56,57]	1.93
	(1 0 0)	0–30 [55]	1530 [56,57]	2.91

Herein, we performed DFT and DFT + U calculations to characterize the interfacial stability and surface activity of MoO_3/γ-Al_2O_3 composites. Composite models consisting of α-MoO_3 (0 1 0) surface on non-spinel and spinel and γ-Al_2O_3 support with (1 0 0) and (1 1 0) surfaces were investigated. The interfacial stability was reported in terms of the interfacial structure, interaction energy, adhesion work, Mulliken charge population, electron density difference, and partial density of states. Fermi softness were used to determine the surface reactivity of the composites. The influence of both the nature of γ-Al_2O_3 support and the surface overage of α-MoO_3 on the surface reactivity were analyzed. In addition, the adsorption and dissociation of H_2S on the surfaces of all ML-composites was studied. The adsorption energies, reaction energy barriers were calculated and compared with the Femi softness. The theoretical investigation may yield valuable clues and essential information to design and synthesis of molybdena/alumina catalysts (see Table 1).

2. Computational details

2.1. Models

The most common and stable crystalline phase of MoO_3 is the orthorhombic α phase, which belongs to the P_{bmn} space group and has the unit cell parameters $a = 3.9628$ Å, $b = 13.855$ Å, and $c = 3.6964$ Å. The α-MoO_3 crystal structure consists of bilayer sheets that stack along the (0 1 0) direction due to the attractive van der Waals forces between them (Fig. 1a). Each bilayer sheet comprises two interwoven planes of corner-sharing MoO_6 octahedron. Adjacent octahedras are edge-sharing, which result in the formation of chains that are cross-linked by oxygen atoms. The perfect α-MoO_3 (0 1 0) surface has three different oxygen sites: a singly bonded terminal oxygen (O_t), asymmetric bi-coordinated bridging oxygen (O_a), and symmetric tri-coordinated bridging oxygen (O_s) [46]. The octahedra in the α-MoO_3 bulk structure are highly distorted, with Mo—O bond lengths ranging from approximately 1.67 Å for the terminal oxygen at the top and bottom of the bilayer sheets to approximately 2.25 Å for the bridging oxygen at the shared edges. In this work, the α-MoO_3 monolayers and bilayers were modeled as 2 × 2 and 3 × 2 periodic supercell slabs of the most stable (0 1 0) surface, respectively.

For the γ-Al_2O_3 support, both non-spinel and spinel structures (Fig. 1b and c) were used due to there are conflicting reports about the γ-Al_2O_3 crystal structure in the literature. Clean ideal surfaces without surface hydroxyl groups were used to model the γ-Al_2O_3 structures [47]. Non-spinel γ-Al_2O_3 belongs to the $P_{21/m}$ space group and has the lattice constants $a = 5.587$, $b = 8.413$, and $c = 8.068$ Å [48,49]. Spinel γ-Al_2O_3 belongs to the F_{d3m} space group and has the lattice constants $a = b = c = 7.911$ Å [50]. The exact locations of the vacancies in the alumina crystal structure are unknown [51,52]. Hence, the γ-Al_2O_3 surface structures were cleaved from the ideal bulk structure to simplify the modeling process. Additionally, neutron diffraction data showed that the γ-Al_2O_3 surfaces are predominantly the (1 1 0) surface (70–83%) with a minor contribution from the (1 0 0) surface (17%) [53,54]. However, the (1 1 0) and (1 0 0) surface energies were calculated by DFT to be 1540 mJ m^{-2} and 970 mJ m^{-2}, respectively [48,49].