

Theoretical Description of Molybdena Based Catalysts; DFT Cluster Model Study.

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Introduction

Molybdenum oxide-based catalysts are active and selective in many catalytic reactions very different types (selective oxidation, oxidative dehydrogenation, isomerization, polymerization, hydrodesulphurization) [1-2]. The catalytic properties of such catalysts strongly depend on acid-base properties of catalysts surfaces, which determine the strength of surface-substrate interactions and facilitate the desorption of products from the surface [3-4]. MoOX systems are particularly good examples for studying the role of different electronic and geometric factors on catalytic properties of the system due to the richness of surface (oxygen and metal) active sites. This richness results from the possibility of different coordination number and oxidation states of Mo and O ions as well as geometrical and chemical environment of surface sites.

Materials and Methods

The electronic properties of the selected (010)MoO₃, (011)MoO₂, (110)MnMoO₄ and (100)β-CoMoO₄ surfaces are examined using the cluster approach (see Fig.1). First, the nucleophilic properties of differently coordinated surface O atoms, which are present at pure (010)MoO₃ surface are discussed. In the next step the results of the creation of local mono- and di-vacancy of O type are studied. In addition, process of surface re-oxidation that leads to the formation of very active surface oxygen species is also investigated. Further, metal reduction states (MoO₃, MoO₂) are studied in order to examine their influence on electronic parameters of oxygen sites. The influence of the additional atoms (Mn, Co) on chemical properties of active sites is examined by the comparison of the electronic structure of cobalt and manganese molybdates (CoMoO₄, MnMoO₄) with the pure Mo-O (MoO₃) system.

The electronic structure of studied system is determined by ab initio density functional theory, using StoBe code. Electron exchange and correlation are described by the gradient corrected (RPBE functional) spin density approximations. For all atoms all electron basis set is used whereas the [Ar]3d¹⁰ core of Mo is approximated by model core potentials. The results are discussed in terms of electronic parameters such as atomic charges, bond orders, total as well as atom projected density of states.

Results and Discussion

The calculations show that the electronic properties and what follows the catalytic reactivity (nucleophilicity) of active sites (lattice or adsorbed) depend on nearest neighbors and the character of bond to metal atom. The nucleophilicity of surface oxygen (measured by atomic charge) scales with the coordination number, bridging oxygen atoms are always more nucleophilic than terminal ones. Theoretical data shows that the creation of oxygen vacancies is connected with considerable relaxation of the surface and in additionally is facilitated by the

presence of H, i.e. by the formation of surface OH/H₂O species that can desorb from the surface more easily than surface oxygen. Molecular oxygen becomes adsorbed (exothermic process) at any surface vacancy, in orientations parallel or perpendicular to the surface. Upon stabilization at the surface, molecular oxygen undergoes activation.

The substitution of molybdenum atom(s) in the clusters by additive atom(s) changes the local electronic state and, what follows, the local reactivity of different surface oxygen sites (Mo=O and Mo-O-X X=Co, Mn) that are present at the catalyst surface. Replacement of Mo by Mn/Co atom decreases the charge/nucleophilicity of oxygen sites, in particular at bridging oxygen sites which are coordinated to these additional elements.

Significance

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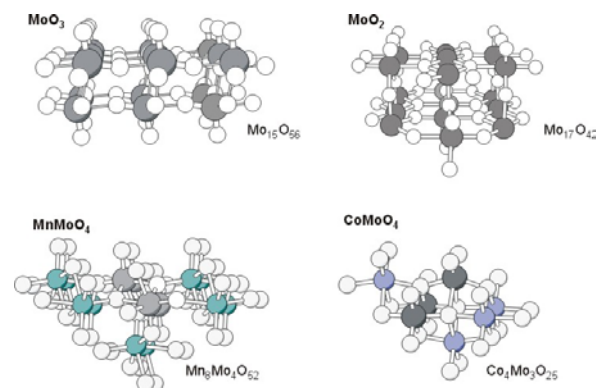


Figure 1. Cluster represented (010)MoO₃, (011)MoO₂, (110)MnMoO₄ and (100)β-CoMoO₄ surfaces. Large grey balls describe Mo, smaller Co or Mn, whereas white oxygen atoms.

References

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