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A DFT study of the electronic structure of cobalt and nickel mono-substituted MoS_2 triangular nanosized clusters

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ABSTRACT

Molybdenum disulfide nanoparticles are of interest for their extensive use in heterogeneous catalysis. Here, we report a systematic density functional theory study carried out to investigate the electronic effects of Co(Ni) mono-substitutions on triangular molybdenum sulfide models of nanometric scale. On the basis of the electronic structure, the charge distribution and the $\Delta(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})$ gap analysis, the triangle molecular model with nickel substitution is identified as more favorable for inducing the best catalytic performance. Nickel consistently induces stronger electronic rearrangements than cobalt, on the molybdenum first-neighbor atoms, which are connected with its higher promoting effect. Charge distribution analysis points out a chemical reduction on the molybdenum sites when the cluster is doped. Moreover, nickel substitution produces smaller $\Delta(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})$ gaps than cobalt substitutions, revealing that Ni-doped clusters are more reactive.

1. Introduction

In recent years environmental regulations have resulted in the demand for ultralow sulfur transport fuels, this fact drives the continuous research and development of new hydrotreating catalysts with higher activity and selectivity. Molybdenum sulfides based catalysts, supported on alumina (MoS_2/Al_2O_3), have been widely used in hydrotreating processes, mainly in the hydrogenation of aromatic compounds and the hydrogenolysis of sulfur from organic compounds present in petroleum (hydrodesulfurization, HDS) [1]. The incorporation of cobalt and nickel into molybdenum sulfides produces promoted catalysts ($Co(Ni)/MoS_2$), that show much higher activities than the corresponding monometallic molybdenum, cobalt or nickel sulfides [1,2].

In order to obtain a detailed description of the role of the catalyst during desulfurization, many aspects of ($Co(Ni)/MoS_2$) structure, properties and activity have been studied from both experimental and theoretical views, useful reviews have been published [3–5]. Key findings were derived from extended X-ray absorption fine structure EXAFS [6–10], Mössbauer emission spectroscopy [11] and IR techniques [12,13], which allowed to identify a Co–Mo–S type structure as the active phase responsible for the promoting effects during the HDS. From these results emerged the view that the Co–Mo–S (and Ni–Mo–S) structures are small MoS_2-like crystallites [14], where promoter atoms decorate the edges of the MoS_2 catalyst and constitutes the active sites.

In the active catalyst, metal centers located at the edges of MoS_2 particles have a local stoichiometry and structure that differs from the catalytically inert basal planes. It has been suggested that Co atoms are located in the Mo plane, likely showing a local coordination different from that of molybdenum in the pure MoS_2. Density functional theory (DFT) simulations have demonstrated that Co and Ni indeed substitutes Mo at the S- or Mo-edge [15] modifying the electronic structure of Mo sites [16].

It has been documented that materials fragmented down to nanoparticles may display new and interesting electronic, as well as structural, features that differ from those exhibited by the bulk system [17]. As a consequence of the new electronic characteristics nanoparticles may adopt unique catalytic properties. Recently, MoS_2 nanoparticles were synthesized in ultrahigh vacuum conditions on Au(1 1 1) nanotemplates, by using scanning tunneling microscopy (STM) atomic resolved structures of unpromoted and promoted MoS_2 have been obtained [18–21]. STM experiments have shown that umpromoted MoS_2 particles take a distinct triangular morphology. Whereas the presence of

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the Co(Ni) promoter implies changes in the morphology of the clusters, Co(Ni)MoS nano-crystallites are closer to a hexagonal shape [22]. Furthermore, STM images have made possible to elucidate the catalytically important edges, estimate the sulfur coverage and the location of sulfur vacancies (coordinatively unsaturated sites, CUS) which are proposed to be the HDS active sites [18].

Despite the many proposals, based on experimental and theoretical approaches, about the nature of the promoting effects, a clear view has not yet been achieved. DFT studies on structural models can be employed to discuss the promoter effects, in terms of the electronic structure of the systems. In the present study we have used density functional theory to investigate the effect of the promoters, cobalt or nickel, on the electronic structure of MoS_2 triangular nanoclusters (Fig. 1). The projected density of states on the atomic sites is analyzed to explore the changes induced by a promoter atom on the Mo first-neighbor sites. Frontier orbital energies of the nanoparticle are also influenced by the presence of cobalt or nickel, thus the analysis of the HOMO–LUMO gap might provide information on the changes in the reactivity of the nanoparticles. Therefore, the catalytic activity of the Co(Ni)/MoS_2 particles can be discussed in relation with these electronic properties, as well as by examining the projected charges on the metal atomic sites, in particular the Hirshfeld partitioning scheme has been employed here for a qualitative analysis, on the influence of the promoters on the molybdenum sites, that should be interpreted in the context of the whole electronic structure features.

2. Computational methods

2.1. Nanoparticle models

MoS_2 nanosize particles, synthesized in ultrahigh vacuum conditions on gold nanotemplates, have been reported to be almost exclusively triangular in shape. For small clusters, the triangles with $n = 4$ or 5 are preferred, n being the number of Mo atoms per side in the cluster [20]. The nanoparticle models used here for the pure system were built up from a S–Mo–S sheet, taking a triangle of 1.58 nm per side with $n = 5$ ($Mo_{15}S_{42}$ stoichiometry) Fig. 1.

As it has been discussed, the presence of promoters implies changes in the morphology of the cluster, being the CoMoS closer to a hexagonal nano-crystallites [22,23]. The focus here is the effect of Co(Ni) mono-substitutions of Mo, therefore the triangular shape model will be employed all along this work. A hexagonal morphology might be considered for models with more substitutions at the edge, however. To model the doped systems each Mo position in the pure cluster was replaced by a Co(Ni) atom at the time, followed by geometry optimization. Given the pure cluster symmetry prior to optimization, there are just four different positions where Co(Ni) can replace Mo in a mono-substitution fashion (see Fig. 1). The Co- and Ni-doped systems have the stoichiometry $CoMo_{14}S_{42}$ and $NiMo_{14}S_{42}$, respectively.

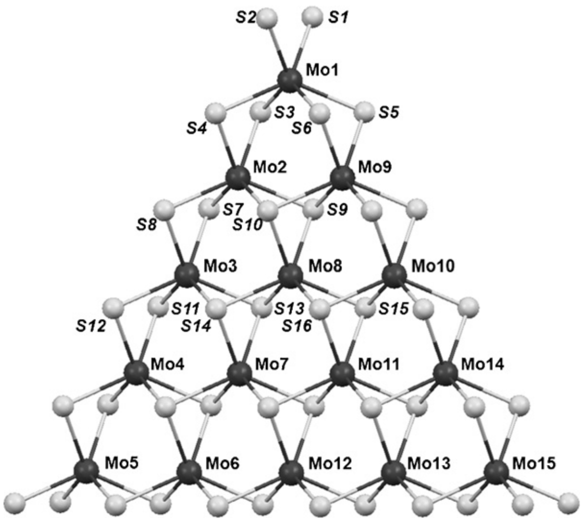

Fig. 1. $Mo_{15}S_{42}$ nanoparticule model. Molybdenum can be substituted by cobalt or nickel at the Mo1 (Co(Ni)@1$Mo_{14}S_{42}$), Mo2 (Co(Ni)@2$Mo_{14}S_{42}$), Mo3 (Co(Ni)@3$Mo_{14}S_{42}$) and Mo8 (Co(Ni)@8$Mo_{14}S_{42}$) sites.

Calculations were run using the supercell approximation ($A = B = 22.162$ and $C = 12.275$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$), each cluster was placed in a supercell large enough to allow for an initial 6.332 Å distance between periodic replica, this precaution avoids spurious interactions between atoms belonging to vicinal cells due to the periodic boundary conditions imposed for the calculations. It has been reported that the maximum activities of Co(Ni)/MoS_2 catalysis are obtained at a Co(Ni)/[Co(Ni) + Mo] ratio close to 0.3, to reach this ratio a model with four doping atoms would be needed, with a mono-substitution scheme the ratio is close to 0.07.

2.2. Density functional theory calculations

Density functional theory (DFT) has been used to determine the geometry and electronic structure of pure, Co- and Ni-doped MoS_2 nanometric models. *Ab initio* computations were carried out using DFT in the generalized gradient approximation (GGA) with the Materials Studio DMol^3 program [24,25] from Accelrys Inc. We employed the revised Perdew–Burke–Ernzerhof (RPBE) exchange-correlation functional [26] with a double numerical plus polarization functions basis set (DNP) to describe the valence electrons, in combination with Hartree-Fock effective core potentials [27,28] for the treatment of the ionic cores. The used real space radii are 4.0, 4.9 and 4.5 Å for sulfur, molybdenum and cobalt(nickel) atoms, respectively. All the systems were relaxed until the remaining total force was below 0.002 Ha/Å, a thermal smearing of 0.05 Ha was used for geometry optimization. For calculating the electronic properties, a more stringent smearing of 0.003 Ha was used to set the orbital occupancy. Spin polarization scheme was applied to all calculations.

3. Results and discussion

3.1. Geometry optimization

Selected metal–sulfur distances, after geometry optimization, are collected in Table 1. We can compare the distances metal–sulfur, in the Mo, Co and Ni coordination spheres, in positions of interest in the pure and doped nanoclusters. Distances in the coordination spheres are shorter for the more exposed sulfurs (edges and corners) than those for the more inner ones. In general, substitution decreases the distance of the more exposed S while increases that of the internal sulfurs; nickel produces bigger changes than cobalt. When substitution is done at the center of the particle (Mo8 site) practically there is no change for nickel, while cobalt produces only a small length reduction. Recent DFT calculations, on the intrinsic properties of MoS_2 triangular sulfur terminated nanoclusters, have proven that the two outermost sulfur atoms are found to contract in the direction perpendicular to the basal plane forming sulfur dimers [20], whereas the length of the core atoms remain practically unchanged relative to the corresponding ones in the bulk [29]. It seems promoter atoms contribute in the same sense; substitution at Mo1, Mo2 and Mo3 sites shorten the S–S distances with respect to the pure system, this fact might help in forming sulfur vacancies.