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RESEARCH NOTE

Influence of Cobalt on a Model of an MoS_2 Hydrodesulfurization Catalyst

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The cluster $Mo_{12}S_{24}$ used as a model of the active phase in hydrodesulfurization (HDS) was submitted to perturbations created by cobalt atoms and studied with density functional theory (DFT). Different molybdenum sites were substituted by cobalt atoms. The results show that the exchange induces strong variations in the charges and significant variations in the bond lengths in the whole cluster. These changes can be correlated with the promoting effect.

Key Words: **density functional theory; hydrotreatment; molybdenum disulfide; cobalt.**

1. INTRODUCTION

Improvement of the hydrodesulfurization (HDS) catalysts has been driven by the need to produce clean fuels, based on the pressing requirements for environmental protection. The most used catalyst for HDS is $Co(Ni)Mo/Al_2O_3$ which consists of well-dispersed molybdenum disulfide nanocrystallites supported by γ-alumina and associated with promoters like Co and Ni. The optimum value of the atomic ratio $Co/(Co + Mo)$, 0.28, was obtained experimentally from catalytic tests (1). Several models were proposed to explain the promoting effect: (i) the contact synergy model (2, 3); (ii) the intercalation and pseudo-intercalation model (4); and (iii) the edge decoration model (5, 6). Unfortunately the experimental characterization techniques yield a picture of the whole sample, but do not provide access to the local structure and to the exact location of the promotor atoms sufficiently to choose between these models. Thus the exact effect of the promotors has never been clearly established. Computational approaches can be used to give some insight into the microscopic processes responsible for HDS, assuming that better knowledge will lead to proposals for improving the catalyst preparation. As the active phases are nanocrystals on the order of about 20 Å, a cluster approach seems reasonable which avoids possible artifacts caused by the periodicity of defects in periodic approaches.

In a previous work the structure of the cluster $Mo_{12}S_{24}$ was optimized with the density functional theory (DFT) method to study its interaction with an alumina support (7) as well as its stability on creation of sulfur vacancies (8). This neutral cluster $Mo_{12}S_{24}$ was found to be representative of the active phase because its size corresponds to the size of the active phase determined by high-resolution electron microscopy (HREM) (9, 10). In the present work the same cluster was used to analyze the influence of the exchange of some Mo by Co atoms.

2. COMPUTATIONAL TECHNIQUE AND MODELS

DFT calculations were performed with the program ADF (11) using the local density approximation (12) and nonlocal corrections (13, 14). The basis set was of double zeta type (DZ) for Mo and Co and double zeta plus polarization (DZP) for S. The computational details were previously described in Ref. (7). Symmetry conditions were applied where possible to reduce the computation time. All calculations were performed on SGI workstations with R4400 and R10000 processors.

The cluster $Mo_{12}S_{24}$ is represented in Fig. 1 with the numeration of the atoms; only the upper layer of sulfur atoms corresponding to the odd atoms is shown. According to the symmetry of the cluster, three types of molybdenum exist: tetracoordinated edge atoms (Mo_1, Mo_2, Mo_6, Mo_9, Mo_{10}, Mo_{12}), outer hexacoordinated Mo atoms (Mo_3, Mo_5, Mo_{11}), and inner hexacoordinated Mo atoms (Mo_4, Mo_7, Mo_8) which hereafter are referred to as the Mo_e, Mo_o, and Mo_i positions, respectively. The calculated models were defined to maintain the possibility of comparison with the unsubstituted cluster. Replacing Mo^{IV} with Co^{2+} means an excess of -2 charge on the cluster and the most obvious choice would have been to calculate $[Mo_{12-x}Co_xS_{24}]^{2x-}$ clusters

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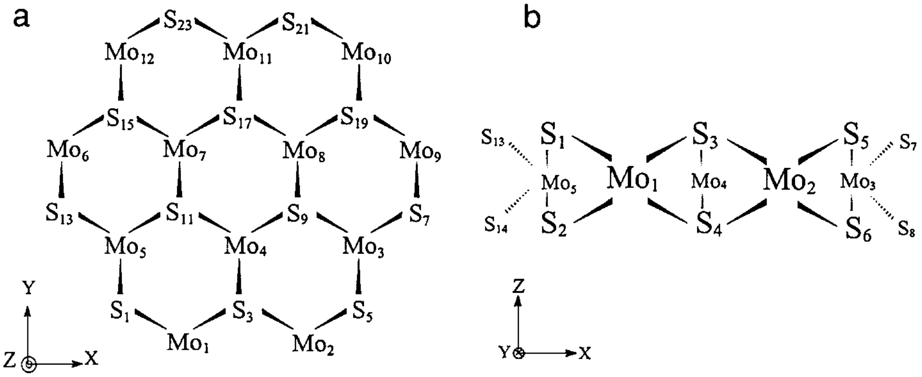

FIG. 1. Cluster $Mo_{12}S_{24}$ used in this study. (a) Projection in the plane *x*0*y* (only the upper layer of sulfur atoms corresponding to the even atoms is shown); according to (b) the parent even S atoms are symmetric to the Mo layer in the negative *z* direction. (b) Projection in the plane *x*0*z*.

(i.e., $Mo_{11}CoS_{24}^{2-}$, $Mo_9Co_3S_{24}^{6-}$). In our preliminary study (7) several clusters were calculated and it turned out that diffuse orbitals are necessary to accommodate the negative charge, particularly when this excess charge is growing as in the $Mo_9Co_3S_{24}^{6-}$ cluster. Therefore we decided to use neutral clusters so that the basis set remains constant for the whole set of calculations. Each Co atom will therefore carry a formal 4+ charge. This assumption could imply that the electronic structure of the cluster is distorted due to the missing electrons; but, on the other hand, this active phase is generally supported on alumina. This support, which is known to have a highly defective structure, is able to buffer the surface charges. Thus the supported active phase is not a charged cluster. Finally it could have been expected that use of a formal Co^{4+} cation would lead to the oxidation of S^{II} to S^{I}; this was not observed at any step of the optimization process (see Section 3) nor by other authors (15). We are therefore confident that this approach allows us access to the general trends of a $CoMo/Al_2O_3$ HDS catalyst.

In a first step one molybdenum atom of each of these sites is replaced by one cobalt atom, leading to three $CoMo_{11}S_{24}$ clusters. After substitution the cobalt atoms have the same nomenclature as the substituted Mo atom. Then the three atoms Mo_3, Mo_5, and Mo_{11} are replaced by cobalt atoms, leading to a symmetric $Co_3Mo_9S_{24}$ cluster. The atomic ratio Co/(Co + Mo) of this last cluster is 0.25, a value corresponding to the optimum experimental ratio 0.28. These models are suitable for analyzing the coordination effects observed by Mössbauer and EXAFS spectroscopy (6, 16).

3. RESULTS AND DISCUSSION

The calculated energies for all systems are gathered in Table 1 where they are compared with the value obtained for the unsubstituted cluster. The exchange in the Mo_1 position is energetically less favorable than any other single substitution, as well as the triple substitution in $Co_3Mo_9S_{24}$. The values calculated for a single substitution in positions Mo_5 and Mo_4 are similar to the values obtained for the creation of a single sulfur vacancy (8). The stability of the structure increases when the cobalt atom is displaced from the edge (Mo_1) to the core of the cluster (Mo_4) over the intermediate position Mo_5. This result is in contradiction with the edge decoration model, but indicates that depending on the preparation method, it is possible to expect different types of substitution leading to metastable catalysts with different electronic properties.

For the triply substituted cluster $Co_3Mo_9S_{24}$ it is possible to calculate the mean energy corresponding to the substitution by one cobalt atom. The value of 4.252 eV is nearly equal to the value for a single substitution in the Mo_4 position. As the single Mo_5 substitution already corresponds to 5.782 eV, the second and third exchanges in positions Mo_3 and Mo_{11} are facilitated by the first, because the mean energy for each of them is only $6.975/2 = 3.488$ eV.

After consideration of the relative stabilities of the clusters it is useful to look at the geometries. The main structural data deduced for the optimized geometry are gathered in Table 2. The MoS and CoS bond lengths correspond to the experimental values for MoS in MoS_2 and CoS in Co_9S_8, respectively (17). As expected, the CoS bond length in the Mo_1 position is shorter than the others, in agreement with the lower coordination number. While the individual variations are rather small when an internal atom like Mo_4 is exchanged, the perturbation caused by substitution of the

TABLE 1

Bonding Energies of the Clusters

Cluster	Exchanged Mo	Bonding energy (eV)
$Mo_{12}S_{24}$	—	−219.719
$CoMo_{11}S_{24}$	Mo_1	−205.035
$CoMo_{11}S_{24}$	Mo_5	−213.937
$CoMo_{11}S_{24}$	Mo_4	−215.477
$Co_3Mo_9S_{24}$	Mo_3, Mo_5, Mo_{11}	−206.962

TABLE 2

Mean Length (Å) of the Different Mo–S and Co–S Bonds

	$Mo_{12}S_{24}$	$CoMo_{11}S_{24}$	$CoMo_{11}S_{24}$	$CoMo_{11}S_{24}$	$Co_3Mo_9S_{24}$
Substituted atoms:	—	Mo_4	Mo_1	Mo_5	Mo_3, Mo_5, Mo_{11}
Bond type[a]					
Mo_i–S_i	2.392	2.390	2.415	2.412	2.408
Mo_i–S_o	2.414	2.435	2.480	2.467	2.491
Mo_o–S_i	2.414	2.419	2.425	2.449	—
Mo_o–S_e	2.380	2.396	2.411	2.416	—
Mo_e–S_o	2.350	2.361	2.385	2.390	2.432
Mo_e–S_e	2.315	2.326	2.331	2.339	2.236
Co_i–S_i	—	2.288	—	—	—
Co_i–S_o	—	2.406	—	—	—
Co_o–S_i	—	—	—	2.356	2.314
Co_o–S_e	—	—	—	2.305	2.319
Co_e–S_o	—	—	2.215	—	—
Co_e–S_e	—	—	2.202	—	—

[a] Subscripts e, o, and i indicate edge, outer, and inner positions of the atoms, respectively.

TABLE 3

Mulliken Charges in the Four Clusters[a]

	$Mo_{12}S_{24}$	$CoMo_{11}S_{24}$ Mo_4	$CoMo_{11}S_{24}$ Mo_1	$CoMo_{11}S_{24}$ Mo_5	$Co_3Mo_9S_{24}$ Mo_3, Mo_5, Mo_{11}
Corner 4-coordinated Mo atoms					
Mo_1	0.603	−10	−71	−10	−35
Mo_2	0.605	−11	−4	−8	−46
Mo_6	0.606	−5	−7	−11	−41
Mo_9	0.608	−4	−8	−8	−48
Mo_{10}	0.605	−6	−7	−8	−36
Mo_{12}	0.607	−5	−8	−8	−48
Outer 6-coordinated Mo atoms					
Mo_3	0.530	−12	−18	−16	−57
Mo_5	0.532	−12	−6	−47	−58
Mo_{11}	0.534	−3	−16	−16	−58
Inner 6-coordinated Mo atoms					
Mo_4	0.586	−16	−18	−18	−24
Mo_7	0.593	−18	−19	−19	−25
Mo_8	0.591	−18	−20	−17	−24
Corner 2-coordinated S atoms					
S_1	−0.325	3	50	33	23
S_5	−0.324	4	19	19	24
S_7	−0.325	6	18	19	24
S_{13}	−0.324	6	17	33	23
S_{21}	−0.325	5	18	18	23
S_{23}	−0.324	5	19	19	24
Outer 3-coordinated S atoms					
S_3	−0.306	14	20	3	39
S_{15}	−0.307	8	0	3	59
S_{19}	−0.309	10	1	0	68
Inner 3-coordinated S atoms					
S_9	−0.210	34	11	10	36
S_{11}	−0.211	34	5	20	35
S_{17}	−0.211	4	12	10	35

[a] Due to the *Cs* symmetry only odd sulfur atoms are reported. The variations are indicated as percentage variations of the charges of the unsubstituted cluster reported in the $Mo_{12}S_{24}$ column (in electronic charges).

external Mo_1 atoms is more significant. The general trend is an increase in the bond lengths indicating a weakening of the bonds. This effect was not observed by Byskov *et al.* (18) for a chain model. Further, these authors reported the formation of S_2^{2-} entities that did not appear at any step of our geometry optimization process. The topology of the substitution sites is different in each model and could be the source of this discrepancy.

The analysis of the Mulliken charges is reported in Table 3. Whatever the Mo atom substituted, modifications of the electronic distribution affect the whole cluster. The most distant atoms have charge variations on the order of 10%. This behavior is in complete opposition to the modifications of the $Mo_{12}S_{24}$ cluster induced by its interaction with a model of alumina (7) or on the creation of vacancies (8). In these studies only the first sphere of coordination surrounding the defect, i.e., the vacancy or the bond with the alumina, was affected. The global effect of the exchange of an Mo atom by a cobalt atom is a decrease in the sum of the positive partial charge carried by the metal atoms from 7.0 to a value between 6.3 and 5.8 electronic charges for the monosubstituted models or 5.5 electronic charges for $Co_3Mo_9S_{24}$. Most of the variation is localized on the cobalt atom which, as expected, tends to reduce its positive charge and is significantly less positive than the exchanged molybdenum. Overall, electrons are transferred from the S to the Co atoms; The positive charges of the Mo atoms decrease by 0.05–0.07 electronic charge over the whole cluster and the absolute values of the sulfur charges also decrease so that the MoS bonds of the cluster become less polar.

4. CONCLUSIONS

The substitution of molybdenum atoms by cobalt in the model cluster $Mo_{12}S_{24}$ leads to unexpected results. The stable configuration corresponds to cobalt atoms substituting Mo atoms in the core of the cluster, while edge cobalt atoms generally proposed as models for the promotion effect are less stable; as such they can also be the most reactive. The surrounding bond lengths of these edge atoms are in good agreement with experimental EXAFS data (16).

The inclusion of a cobalt atom in a structure creates an electrophilic site and induces variations that are smeared over the whole cluster; this behavior is completely in opposition to the local character of all perturbations applied to this cluster in former works (7, 8). The effects are an increase in the bond lengths corresponding to their weakening and a decrease in the polar character of the MoS bonds. Both results may partly explain the promoting effect. But they presently do not permit discussion of the optimum atomic ratio Co/(Mo + Co) observed around 28% in catalytic tests, because other configurations should be calculated. But the electronic structure of the cluster is strongly modified by the Mo/Co exchange. We can therefore expect that the creation of coordinative unsaturated sites (CUS) by elimination of sulfur atoms, as well as the properties of these CUS, will be affected by the presence of Co atoms. Their interaction with products like thiophene and hydrogen during HDS will also be affected.

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