Edge termination of MoS_2 and CoMoS catalyst particles

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The edge termination of MoS_2 and CoMoS catalyst particles is studied by density functional calculations. We show that for structures without vacancies Mo-terminated edges have the lowest edge energies. Creation of vacancies, which are believed to be active sites in these catalyst systems, leads to structures having mainly S-terminated edges. Thus, the results indicate that the shape of the MoS_2 and CoMoS structures may be a dynamical function of the reaction conditions. Independent of the type of edge termination, the results indicate that triangular-shaped nanocrystals may be expected in order to maximize the exposure of the favored edges. This is in contrast to the commonly assumed hexagonal morphology, but triangular-shaped MoS_2 structures have in fact recently been observed in STM studies of model systems [1].

Keywords: hydrotreating, edge termination, MoS_2, CoMoS, density functional calculations, triangular structure

1. Introduction

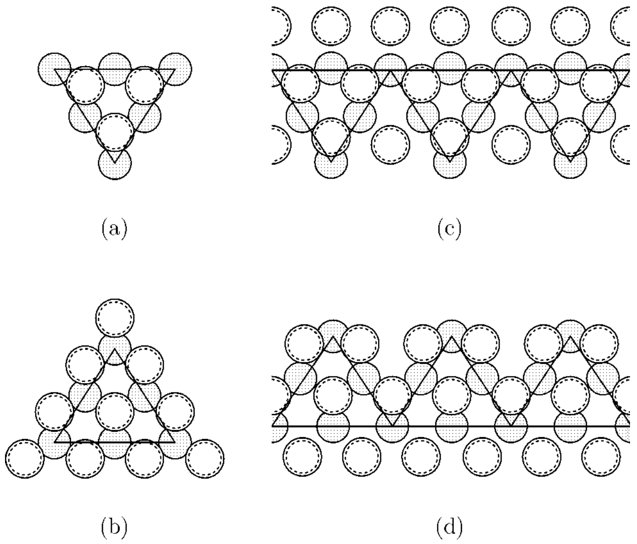
The commonly used industrial hydrotreating catalysts for sulfur removal from oil fractions are based on Mo structures with Co or Ni added as a promoter [2]. The catalyst consists of small particles of MoS_2, where Mo atoms are sandwiched between two hexagonal close-packed S layers. Two-dimensional structures consisting of single S–Mo–S layers are observed in Al-supported catalysts after typical sulfiding procedures [2–5]. The size of these crystallites is typically 1–3 nm [2,6,7]. The reactivity of the catalyst has been found to be related to the edges rather than the basal plane of MoS_2 [2,8–10]. The promoter atoms occupy sites at the edges of the so-called CoMoS structures which leads to an increased reactivity compared to the pure Mo edge sites [11]. Coordinatively unsaturated sites (CUS) along the edges of the catalyst particles are believed to provide the active sites, where molecules can adsorb and undergo further reactions. Based on effective medium theory studies [12] and more recently density functional theory (DFT) calculations [13], it has been suggested that one role of the Co and Ni promoters is to facilitate making coordinatively unsaturated metal sites by reducing the sulfur binding energy at the edge. If the edge sulfur atoms are bound weaker, the equilibrium concentration under a certain H_2/H_2S ratio in the gas phase will be smaller and the number of active sites correspondingly larger.

With the exception of recent scanning tunneling microscopy (STM) studies of MoS_2 nanostructures [1], the large experimental and theoretical efforts have not established much insight into the morphology of alumina-supported MoS_2 structures [2]. Many shapes have been considered [2,14] but most models have assumed hexagonal geometry [15]. The MoS_2 can essentially have two different edge terminations, the Mo($10\bar{1}0$) and S($\bar{1}010$) edges. It is expected that their equilibrium shape will be determined by the relative edge energies, which may furthermore depend on the edge concentration of S adatoms, and hence on temperature and gas-phase composition and on the presence of Co or Ni edge atoms.

In the present letter, we apply DFT calculations to a simple model system in order to shed further light on the shape of small unpromoted and Co-promoted MoS_2 particles with and without S vacancies at the edges. We show that for our model system there is a strong tendency to form Mo-terminated ($10\bar{1}0$) edges for both the pure MoS_2 and the CoMoS systems when no vacancies are present, but in the presence of vacancies this tendency is reversed, so that predominantly S-terminated ($\bar{1}010$) edges are exposed. This means that for the Co-promoted system, where vacancies are more easily formed than on non-promoted edges [13], the S-terminated edges may become the most stable.

2. Calculational details

The present study is based on a set of calculations of the energetics of MoS_2-based structures using density functional theory (DFT) [16,17]. The calculations are parameter free and exchange–correlation effects are treated nonlocally by use of the generalized gradient approximation (GGA) [18]. The wave functions are expanded in plane waves [19] with a cutoff energy of 25 Ry, and the ionic cores are treated with ultra-soft pseudo-potentials (US-PP) [20]. The calculations are performed self-consistently with 3 k-points in the irreducible Brillouin zone (IBZ). Periodic boundary conditions are applied and the structures are described as slabs. For each structure studied, the atomic positions are relaxed in order to obtain the minimum energy configuration.


(a) (c)

(b) (d)

Figure 1. Illustration of catalyst particles with different edges: (a) Mo termination and (b) S termination. The periodic triangular structures used in the present calculations: (c) Mo termination and (d) S termination. Color codes: white (S) and light grey (Mo). Dashed circles indicate S atoms in the bottom layer.

The main focus in the present work is on the relative stability of the edges of the catalyst particles, i.e., whether Mo- or S-terminated edges are predominant. The question can be answered by investigating which of the triangular structures shown in figure 1 (a) and (b) is most stable. The structure in (a) only exposes the Mo edge, while the one shown in (b) only has S edges. In the present calculational scheme it is computationally simpler to study the periodic triangular structures shown in figure 1 (c) and (d). They differ from the ones in figure 1 (a) and (b) by sharing the metal atoms in the corners of the basal plane of the triangles. This implies that the results should only be taken as indicative of the relative stability of the two structures.

3. Results and discussion

In the calculations, we first consider the relative stability of the two structures in figure 1 (c) and (d) for three different setups: (i) pure MoS_2 with a number of S atoms at the edges, (ii) the same structure with one of the Mo edge atoms substituted by Co, and (iii) the CoMoS structure with S vacancies.

The calculated equilibrium structures and energy differences are shown in table 1. The energy difference, ΔE, is defined as

$$\Delta E = E_{\text{tot}} - E_{\text{ref}}, \tag{1}$$

where E_{tot} is the calculated total energy of the particular structure and E_{ref} is the total energy of the Mo edge structure. If ΔE in equation (1) is positive the Mo edge type is the more stable; if ΔE is negative the S edge is the more stable type. Each Mo edge–S edge set, i.e., a and b in (i), c and d in (ii), and e and f in (iii), can directly be compared due to the same amount of the different species.

In structures a, c, and e, a metal atom (either Mo or Co) has been placed at the tip of the indicated triangle in table 1, i.e., bonded to two S atoms, cf. figure 1(c). However, after relaxation the metal atom has in all cases moved to a position where it bonds to three or four S atoms, as shown in the top views of configurations a, c, and e. The movement by the metal atom is most likely done in order to maximize the coordination number (here from the S atoms).

Structures without vacancies are a–d in table 1. The difference in total energy between the two MoS_2 type structures, a and b, is 0.88 eV, meaning that structure a is more stable by this amount. The energy difference between the two CoMoS microcrystals without vacancies is 0.93 eV, with c being the more stable one. We therefore see for structures without vacancies that formation of Mo-terminated $(10\bar{1}0)$ edges is favored (a and c).

A comparison of the structures with vacancies, see e and f in table 1, reveals f to be more stable by 0.63 eV. Hence, creation of vacancies changes the picture; now crystallites with S-terminated $(\bar{1}010)$ edges are energetically more stable. These CoMoS type particles exposing vacancies or active sites are probably the ones active in hydrotreating reactions.

Secondly, we investigate whether the MoS_2 microcrystals are more reduced or sulfided than the ones shown in table 1. Adding the maximum number of sulfur atoms to the presented microcrystals results in structures with the ratio of $\mathrm{Mo:S} = 5:14$, as depicted in table 2.

Since configurations g and h have the same amount of Mo and S atoms the energy difference, ΔE, defined in equation (1) can be applied. In this case, E_{ref} is -6499.84 eV and ΔE is seen to be positive meaning that the Mo edge type is the more stable one, as in the case of the MoS_2 structures in table 1.

To determine the state of sulfidation of the MoS_2 microcrystal, we compare the two Mo edge type configurations, a and g, with two more reduced structures, i and j, shown in table 3. Due to the different Mo : S ratios for the four structures, we consider the following reaction which ensures conservation of the number of Mo and S atoms:

$$\mathrm{Mo_5S}_x + (y-x)\mathrm{H_2S} \rightarrow \mathrm{Mo_5S}_y + (y-x)\mathrm{H_2} \tag{2}$$

where x and y are the numbers of S atoms in the MoS_2 configuration before and after reaction (2), respectively. The corresponding energy difference is given by

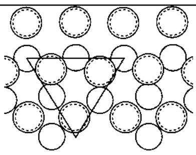
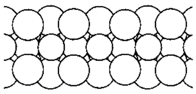
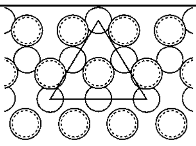
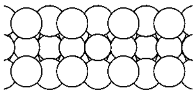
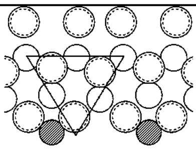
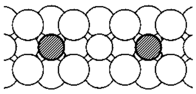
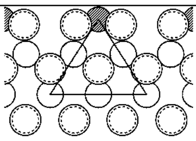
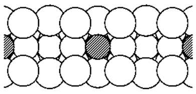
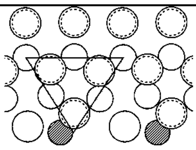
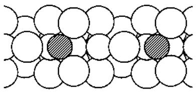
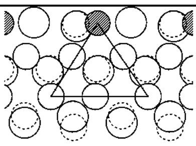
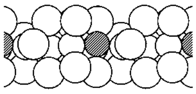
$$\begin{aligned}\Delta E_{x,y} = {} & E(\mathrm{Mo_5S}_y) - E(\mathrm{Mo_5S}_x) \\ & + (y-x)\big(E(\mathrm{H_2}) - E(\mathrm{H_2S})\big),\end{aligned} \tag{3}$$

where a negative sign of $\Delta E_{x,y}$ implies the more sulfided structure, $\mathrm{Mo_5S}_y$, to be the more stable one and a positive sign the opposite. The results collected in table 4 reveal the most sulfided MoS_2 configuration to be the most stable one. This structure g is more stable than the most reduced of the studied, configuration j, by around 8 eV.

Structure g can furthermore be reduced by removing one S atom per sulfur dimer in the row of dimers at the edge,

Table 1

MoS_2 and CoMoS structures exposing two different types of microfacets: Mo- and S-terminated edges. The microcrystals are indicated by triangles. Structures are all shown after relaxation. Color codes: white (S), light grey (Mo), and dark grey (Co). Energy differences are listed. The value of E_{ref} is (i) −5855.03, (ii) −6548.21, and (iii) −6225.56 eV.

i) MoS_2, No Vacancies				
	Edge Type	Top View	Side View	ΔE (eV)
a	Mo Edge			0
b	S Edge			+ 0.88
ii) CoMoS, No Vacancies				
	Edge Type	Top View	Side View	ΔE (eV)
c	Mo Edge			0
d	S Edge			+ 0.93
iii) CoMoS, With Vacancies				
	Edge Type	Top View	Side View	ΔE (eV)
e	Mo Edge			0
f	S Edge			− 0.63

whereby configuration k depicted in table 3 emerges. It is seen that the remaining sulfur atoms from the dimers have moved half a lattice constant, probably in order to maximize the coordination number of the edge Mo atoms. These S atoms have furthermore moved up in the plane of the Mo atoms. Structure k is found to be only 0.21 eV per S atom less stable than g, again making the Mo edge type more stable than the S edge structure h in table 2. Hence in addition to g, configuration k can exist.

Finally, from table 4 it is seen that g is more stable than a by 1.21 eV which is the cost of removing the S dimer from the tip of the "Mo triangle" in the MoS_2 structure. The energy required to remove a S dimer from the tip of the "S triangle", going from b to h (see table 4), is a bit less: 1.08 eV. Hence, for Mo as well as S edge type structures it is energetically quite expensive to create a vacancy at a corner site.

4. Conclusion

In the present study simple model structures of unpromoted and Co-promoted catalyst particles are considered. The crystallites are 0.1–1 nm in "diameter" (i.e., across the chain). Effects at corner sites may influence the results, but we cannot at this time judge how severe this problem is. Interactions with the support (usually alumina oxide, γ-Al_2O_3) have not been included here either. The interaction with the support may take place predominantly through one of the edges [21] and this may induce the presence of

Table 2

Completely sulfided MoS_2 structures exposing two different types of microfacets: Mo- and S-terminated edges. The microcrystals are indicated by triangles. Structures are all shown after relaxation. Color codes: white (S) and light grey (Mo). Energy differences are listed.

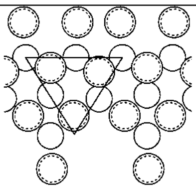
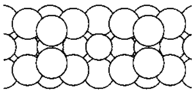
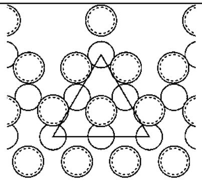
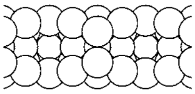
MoS_2, Completely Sulfided				
	Edge Type	Top View	Side View	ΔE (eV)
g	Mo Edge			0
h	S Edge			+ 1.01

Table 3

Reduced MoS_2 structures with Mo-terminated edges. The microcrystals are indicated by triangles. Structures are all shown after relaxation. Color codes: white (S) and light grey (Mo).

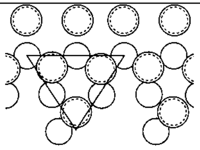
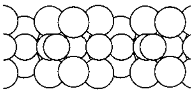
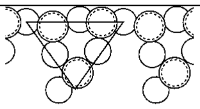
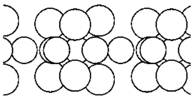
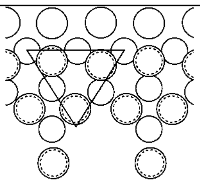
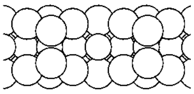
MoS_2, Reduced			
	Edge Type	Top View	Side View
i	Mo Edge		
j	Mo Edge		
k	Mo Edge		

Table 4

MoS_2 structures with different Mo : S ratios. The numbers of S atoms in the MoS_2 configuration before and after reaction (2) are given by x and y. The energy difference, $\Delta E_{x,y}$, is defined in equation (3).

Mo_5S_x	Mo_5S_y	x	y	$\Delta E_{x,y}$ (eV)
MoS_2, Mo edge type				
j	i	6	10	−2.60
i	a	10	12	−4.18
a	g	12	14	−1.21
MoS_2, S edge type				
b	h	12	14	−1.08

a particular edge even if it is not the most stable for the free particle.

In spite of the shortcomings of the model, the relative stability of the edges can be studied. We conclude that there is evidence for Mo edges dominating the pure MoS_2 particles, while the (Co-decorated) S edges of the CoMoS particles are favored during turnover conditions. The triangular structures are seen to reshape when the H_2/H_2S ratio is changed. This indicates that the shape of the catalyst platelets may be a dynamical function of the reaction conditions.

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