



Density-functional theory (DFT) study of arsenic poisoning of NiMoS

Shaofeng Yang^a, John Adjaye^b, William C. McCaffrey^a, Alan E. Nelson^{a,*}

^a Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

^b Syncrude Canada Ltd, Edmonton Research Centre, Edmonton, Alberta, Canada T6N 1H4

ARTICLE INFO

Article history:

Received 9 December 2009

Received in revised form 1 February 2010

Accepted 2 February 2010

Available online 10 February 2010

Keywords:

Density-functional theory

Nickel-promoted molybdenum sulfide

Hydrotreating

Organoarsenic

Deactivation

ABSTRACT

Arsenic poisoning of NiMoS hydrotreating catalysts was studied using density-functional theory (DFT) calculations. The incorporation of arsenic into NiMoS by chemical adsorption and dissociation of organoarsenic molecules (AsH_3 , $(\text{CH}_3)_3\text{As}$, $(\text{C}_2\text{H}_5)_3\text{As}$, and $(\text{C}_6\text{H}_5)_3\text{As}$) and the substitution of Ni and S atoms by arsenic on both fully promoted Ni(1 0 0)Mo- and Ni(1 0 0)S-edge surfaces were investigated. DFT calculation results show that the adsorption of organoarsenic compounds is energetically favored on both surfaces and there is a correlation between the adsorptivity of the arsenic compounds and their electronic structure. After the organoarsenic molecules have adsorbed on the edge surfaces, dissociation on a Ni(1 0 0)S-edge surface is energetically favored. Arsenic may substitute Ni atoms on both Ni(1 0 0)Mo-edge and Ni(1 0 0)S-edge surfaces. However, the substitution of S atoms by arsenic may only occur on the Ni(1 0 0)S-edge surface. The DFT results are compared with previously reported EXAFS studies on arsenic deposited NiMoP/Al₂O₃ hydrotreating catalysts.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Nickel-promoted molybdenum sulfide (NiMoS) catalysts have been widely used in hydrotreating processes of various oil fractions. The presence of arsenic as arsine and organoarsenic compounds in petroleum has been recognized to have a significant impact on catalyst activity [1–6]. The significance of arsenic deactivation can be evidenced by the fact that an arsenic sorbent material is often installed in a guard reactor in order to prevent arsenic contacting the NiMoS hydrotreating catalyst. The arsenic sorbent is typically a supported transition metal sulfide with an efficacy to chemically adsorb arsenic present in the feed stream. Current arsenic removal sorbents are comprised of Ni–Mo supported on Al₂O₃ [2], and effectively remove arsenic from naphtha by sacrificing the nickel to form Ni_xAs_y. However, arsenic can remain in the guard reactor effluent either through incomplete sequestering of the arsenic in the guard reactor or by leaching of arsenic from the sorbent material. The effect can be pronounced with the accumulation of arsenic in the top bed of the naphtha hydrotreater within several months of operation.

Arsenic is present in many crude oils in low ppm or ppb levels [3]. Compared with the deactivation due to coke and nickel and vanadium metals, deactivation of NiMoS hydrotreating catalysts

by arsenic is less frequently studied. Several recent studies have reported the deactivation of Ni/Al₂O₃ catalysts using an artificially arsenic concentrated feed stream. These studies have demonstrated that on a Ni/Al₂O₃ catalyst, deactivation proceeds via a stepwise process by the initial population of surface arsenic atoms, the diffusion of these arsenic atoms into the supported nickel particles to form intermetallic Ni_xAs_y phases, and the final formation of crystalline NiAs [4,5]. Additionally, studies using nickel reforming catalysts have also discussed the formation of Ni₅As₂ and NiAs nickeline alloy phases [6]. However, information regarding the mechanism and chemical state of arsenic after deposition on a NiMoS hydrotreating catalyst is scarce. Considering the significantly lower amount of nickel in the NiMoS hydrotreating catalyst and the unique structure of the bimetallic NiMoS phase, the deactivation mechanism of NiMoS is expected to be considerably different than the mechanism for highly loaded Ni/Al₂O₃ catalysts. Furthermore, Puig-Molina et al. [7] have questioned the formation of Ni_xAs_y as evidenced by sulfur–arsenic bonding in NiMoP hydrotreating catalysts. Their EXAFS results do not support the existence of Ni–As bonding, either as intermetallic Ni_xAs_y phases or poisoned Ni edge sites by chemisorbed arsenic [7]. Thus, the need to clarify these issues and understand the deactivation mechanism and energetics of NiMoS by arsenic is of fundamental importance for the hydrotreatment of arsenic containing petroleum.

Molecular modeling and computational investigations have made important contributions towards understanding the structures and properties of molybdenum-based hydrotreating catalysts [8–25], such as the equilibrium sulfur coverage on the edge planes of promoted and unpromoted MoS₂ catalysts [9–11], the ener-

* Corresponding author. Current address: The Dow Chemical Company, Corporate Research and Development, Midland, MI 48674, USA. Tel.: +1 989 638 3525; fax: +1 989 638 9674.

E-mail address: aelnson@dow.com (A.E. Nelson).

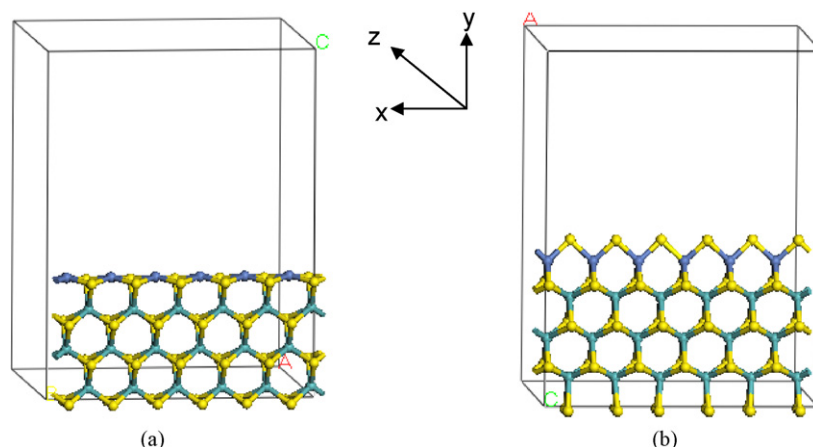


Fig. 1. Periodic models of MoS₂: (a) Ni(100)Mo-edge, (b) Ni(100)S-edge.

getically favorable locations of promoter (Ni, Co) atoms [12,13], the adsorption and activation of hydrogen on various edge surfaces [14–19], the adsorption of sulfur compounds on unpromoted edge surfaces of MoS₂ catalysts [20–23], and the adsorption of nitrogen compounds on nickel-promoted molybdenum sulfide (NiMoS) catalysts [24,25]. In this research molecular simulation (density-functional theory) is utilized to develop a comprehensive understanding of NiMoS catalyst deactivation mechanisms and energetics due to arsenic accumulation. The adsorption of AsH₃, (CH₃)₃As, (C₂H₅)₃As and (C₆H₅)₃As are studied on both fully promoted Ni(100)Mo-edge and Ni(100)S-edge surfaces, and the energetics of adsorption and dissociation provide new insights into the deactivation of NiMoS by organoarsenic compounds.

2. Methods

2.1. Models of catalyst and organoarsenic compounds

The NiMoS catalyst model used in the present study is shown in Fig. 1, in which molybdenum atoms on the MoS₂ (10 $\bar{1}$ 0) Mo-edge (Fig. 1a) and (10 $\bar{1}$ 0) S-edge (Fig. 1b) surface have been substituted by nickel atoms to obtain the fully nickel-promoted catalyst surface, termed the Ni(100)Mo-edge and the Ni(100)S-edge, respectively. The model is repeated in x-direction with a periodicity of six MoS₂ units, and separated by vacuum layers of 15 Å in the y- and z-directions. The volume of the unit supercell is 19.0 × 24.6 × 18.4 Å. In the large supercell, the interaction between the organoarsenic molecules and the catalyst surface will not be affected by molecules in the neighboring cells. Four model organoarsenic compounds, AsH₃, (CH₃)₃As, (C₂H₅)₃As and (C₆H₅)₃As, are used in this study. The boiling point of these four compounds ranges from –62.5 °C (AsH₃) to 360 °C (C₆H₅)₃As.

2.2. DFT calculations

The energy calculations are based on density-functional theory (DFT), and have been performed using Materials Studio DMol³ from Accelrys® (version 4.0). The electronic wave functions are expanded in numerical atomic basis sets defined on an atomic-centered spherical polar mesh. The double-numerical plus polarization functions (DNP) and Becke exchange [26] plus Perdew–Wang approximation [27] non-local functionals (GGA-PW91) are used in all calculations. The real space cutoff radius is 4.4 Å. All electron basis sets are used for light elements, such as hydrogen, carbon, and sulfur. Effective core potentials [28,29] are used to treat core electrons of molybdenum, nickel and arsenic and a *k*-point of (1 × 1 × 1) was used because of the large supercell.

Spin polarization was applied to all calculations for the systems containing nickel.

2.3. Thermodynamic calculations

The calculations of energy changes are given with the incorporation of AsH₃ on the catalyst surface as an example. The adsorption energy of AsH₃ ($\Delta E_{\text{ads,AsH}_3}$) on an edge surface is calculated according to the following equation;

$$\Delta E_{\text{ads,AsH}_3} = E_{\text{surface,nAsH}_3} - E_{\text{clean surface}} - nE_{\text{AsH}_3} \quad (1)$$

where $E_{\text{surface,nAsH}_3}$, $E_{\text{clean surface}}$, and E_{AsH_3} represents total electronic energies of an edge surface with *n* adsorbed AsH₃ molecules, the clean surface, and free AsH₃ molecule at 0 K, respectively. In addition to molecular adsorption on the surface, AsH₃ molecule can also dissociate to form an adsorbed arsenic atom and gas-phase molecular hydrogen, in which case the dissociation energy ($\Delta E_{\text{dis,AsH}_3}$) is calculated by the following equation;

$$\Delta E_{\text{dis,AsH}_3} = E_{\text{surface,nAs}} + \left(\frac{3}{2}n\right)E_{\text{H}_2} - E_{\text{clean surface}} - nE_{\text{AsH}_3} \quad (2)$$

where $E_{\text{surface,nAs}}$ represents the total electronic energy of an edge surface with *n* As atoms adsorbed. Another possible mechanism for arsenic to incorporate into NiMoS is to substitute Ni or S atoms. The energy change for the substitution of Ni by As atom ($\Delta E_{\text{sub,Ni}}$) is calculated by the following equation, with NiAs and gas-phase molecular H₂ as energy references

$$\Delta E_{\text{sub,Ni}} = E_{\text{surface(nAs)}} + E_{\text{NiAs}} + 3nE_{\text{H}_2} - E_{\text{clean surface}} - 2nE_{\text{AsH}_3} \quad (3)$$

where $E_{\text{surface(nAs)}}$ represents the total electronic energy of an edge surface with *n* Ni atoms being substituted by *n* As atoms. The energy change for the substitution of S atoms ($\Delta E_{\text{sub,S}}$) on the edge surface of NiMoS is calculated by the following equation, with gas-phase molecular H₂S and H₂ as energy references

$$\Delta E_{\text{sub,S}} = E_{\text{surface(nAs)*}} + nE_{\text{H}_2\text{S}} + \left(\frac{n}{2}\right)E_{\text{H}_2} - E_{\text{clean surface}} - nE_{\text{AsH}_3} \quad (4)$$

where $E_{\text{surface(nAs)*}}$ represents the total electronic energy of an edge surface with *n* S atoms being substituted by *n* As atoms. These energy changes defined in Eqs. (1)–(4) were used to evaluate the relative stabilities of different surfaces. Corresponding free energy changes for the adsorption of organoarsenic molecules can be calculated by adding temperature correction and partial pressure

terms [13,17,19]. The free energy changes of the adsorption process of arsenic compounds on the surface can be calculated as follows.

$$\Delta G_{\text{ads,AsH}_3} = \Delta E_{\text{ads,AsH}_3} + \Delta G_{\text{TCorr}}^0 - RT \ln p_{\text{AsH}_3} \quad (5)$$

The energy calculations for the incorporation of other representative organoarsenic molecules were performed using a similar methodology.

3. Results and discussion

3.1. Location of nickel in NiMoS

It is generally believed that a Ni–Mo–S phase exists in NiMoS catalyst with a structure similar to Co–Mo–S, in which Co atoms are located at the edge positions of MoS₂ nanostructures, as observed by Lauritsen et al. using scanning tunneling microscopy (STM) [30]. No direct experimental information was available on the location of the Ni promoters in NiMoS until STM studies on NiMoS nanoclusters were carried by Lauritsen et al. in 2007 [31]. Theoretical studies based on slab models [9,11,13] or calculations of cluster structures [12] have been used to investigate the incorporation of Ni at the MoS₂ edges, and such studies have also provided information on the sulfur coverage at the edges under experimental and reaction conditions. Studies of Schweiger et al. [12] and Sun et al. [13] have shown that Ni thermodynamically prefers the metal edge of the MoS₂ slab under typical sulfidation conditions. It should be noted, however, that these studies do not exclude the location of Ni on the S-edge, notwithstanding that such a location may be less abundant [13]. On the other hand, the most recent STM studies carried by Lauritsen et al. showed that on an Au(1 1 1) surface, the location of Ni sites depends on the size of NiMoS nanocluster [31]. Larger clusters exhibited a truncated triangular shape, similar to that for CoMoS nanoclusters, exposing the unpromoted (1 0 $\bar{1}$ 0) metal edges with a 100% S coverage and the fully Ni-substituted ($\bar{1}$ 0 1 0) S edges with a 50% S coverage. Smaller clusters show dodecagonal shapes terminated by three different edges, all of which contain Ni-promoter atoms fully or partially substituting the Mo atoms. Moreover, most commercial hydrotreating catalysts consist of promoted MoS₂ particles distributed on a high surface area support, and many parameters such as the kinetics of the formation of the active phases during the sulfidation or sulfide-support interactions play an important role on the final structure of the sulfide phase [32]. Hence, in this study, the location of Ni on both edges has been considered for the incorporation of arsenic into NiMoS catalyst.

3.2. Incorporation of arsenic into the Ni(1 0 0)Mo-edge (1 0 $\bar{1}$ 0) surface

Substitution of all molybdenum atoms on the MoS₂ (1 0 $\bar{1}$ 0) edge surface by nickel atoms produces a fully nickel-promoted catalyst surface, termed the Ni(1 0 0)Mo-edge. The bare Ni(1 0 0)Mo-edge is the most stable structure for NiMoS catalyst at typical hydrotreating reaction conditions [13].

3.2.1. Adsorption of organoarsenic compounds

The adsorption of AsH₃, (CH₃)₃As, (C₂H₅)₃As and (C₆H₅)₃As on a fully nickel-promoted surface are summarized in Table 1. Calculation results show that the adsorption of arsenic compounds on nickel sites is energetically favored on the Ni(1 0 0)Mo-edge surface. The highly negative ΔE_{ads} values indicate the strong adsorption strength of organoarsenic compounds on this surface. When there are three AsH₃ molecules adsorbed on the surface (structure 1e), the adsorption energy is reduced from –1.68 to –1.32 eV/As because of the repulsion effect between the adsorbates. The adsorption of arsenic compounds does not occur on

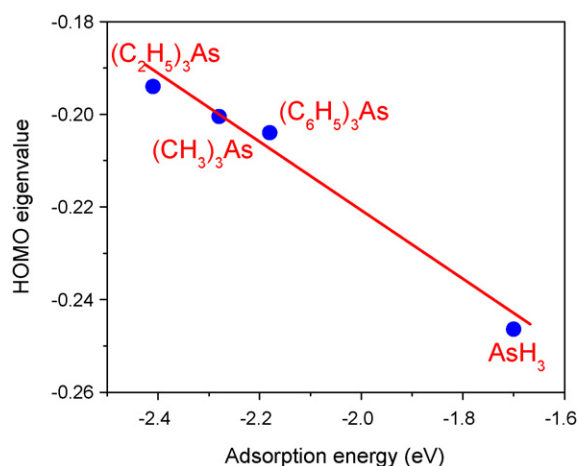


Fig. 2. Correlation between the adsorption energies on Ni(1 0 0)Mo-edge surface and the eigenvalues (in Hartrees) of the HOMO of arsenic compounds.

the S sites of the Ni(1 0 0)Mo-edge surface; when organoarsenic molecules are initially put on top of S atoms, they moved to the top of Ni atoms after geometry optimization.

The adsorption energies of arsenic compounds vary with the different As ligands (substituents of H in AsH₃). The adsorption energy increases in the order of AsH₃ < (CH₃)₃As < (C₂H₅)₃As, while the adsorption energy of (C₆H₅)₃As is lower than that of (CH₃)₃As and (C₂H₅)₃As. It seems that there is a correlation between the adsorptivity of the arsenic compounds and their electronic properties. Fig. 2 shows the correlation between the adsorption energies and the eigenvalues of the highest occupied molecular orbital (HOMO) of arsenic compounds. The absolute value of the adsorption energy increases with the increase of the HOMO eigenvalue. When arsenic compounds are adsorbed on the Ni(1 0 0)Mo-edge surface, the electrons from the HOMOs of the molecules may transfer to the unoccupied states of the active sites. The higher energy level of the HOMO makes it easier for the arsenic molecules to donate electrons and therefore results in a higher adsorption energy. The electronic properties of the bare surface and surfaces with adsorbed arsenic molecules are also calculated. Fig. 3a shows the local projected density of *d*-states on nickel sites of the bare Ni(1 0 0)Mo-edge surface and surfaces with one and three AsH₃ molecules. The adsorption of AsH₃ molecules increased the density of the occupied states below the Fermi level, which also suggested that electrons are transferred from arsenic to the nickel sites on the Ni(1 0 0)Mo-edge surface. Fig. 3b shows the local projected density of *d*-states on a single nickel site of the bare Ni(1 0 0)Mo-edge surface and surfaces with indicated arsenic molecules adsorbed on top of this nickel site. The adsorption of all these four arsenic molecules increased the density of the occupied states of the nickel site below the Fermi level. In addition, the positive Mulliken charges of the nickel atoms on the Ni(1 0 0)Mo-edge surface and the negative charges of arsenic atoms in AsH₃ decreased when AsH₃ is adsorbed on the Ni-edge surface. All these results indicate that the adsorption of arsenic compounds on the Ni-edge is (or is partly) stabilized by arsenic donating electrons to the Ni(1 0 0)Mo-edge surface.

3.2.2. Dissociation of organoarsenic compounds

A previous study on arsine poisoning of a Ni/Al₂O₃ catalyst showed that the adsorption of arsine is dissociative and heating of arsine-covered nickel surfaces leads to the desorption of hydrogen formed and the appearance of arsenic–nickel clusters [33]. In the arsenic–nickel clusters, arsenic interacts with a larger number of nickel atoms than when arsenic is in the surface adsorbed state. A study on the reaction kinetics of Ni/Al₂O₃ with the substituted

Table 1
Surface configurations of organoarsenic adsorption on the Ni(1 0 0)Mo-edge surface after optimization and the relative energies of optimized configurations with the clean surface and gas-phase molecule as the energetic references.

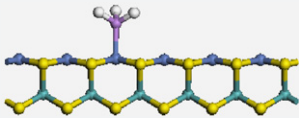
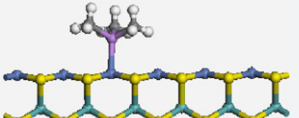
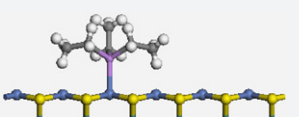
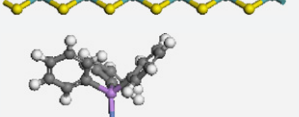
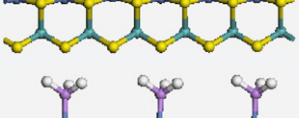
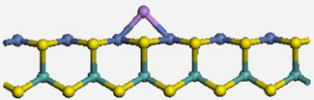
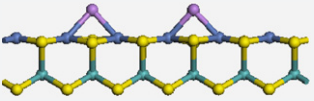
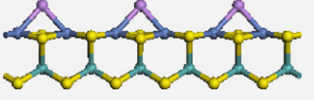
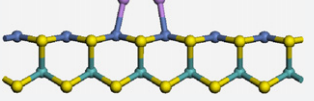
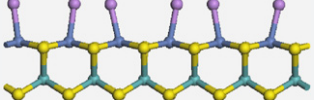
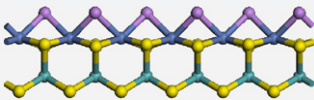
Configurations	Arsenic compounds	Optimized structure	ΔE_{ads} (eV/As)
1a	AsH ₃		−1.70
1b	(CH ₃) ₃ As		−2.28
1c	(C ₂ H ₅) ₃ As		−2.41
1d	(C ₆ H ₅) ₃ As		−2.18
1e	AsH ₃		−1.32

Table 2
Surface configurations and relative energies of AsH₃ dissociation on the Ni(1 0 0)Mo-edge surface. The value of ΔE_{dis} was calculated by Eq. (2).

Configurations	Optimized structure	ΔE_{dis} (eV/As)
2a		−0.34
2b		−0.32
2c		−0.28
2d		−0.40
2e		−0.40
2f		−0.40

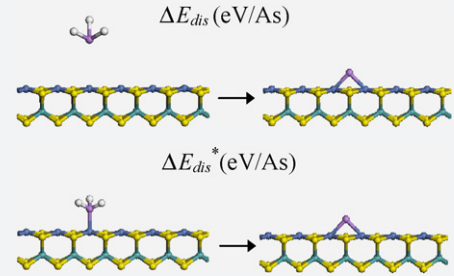
arsine, (C₆H₅)₃As, showed that between 100 and 200 °C and H₂ pressures of 0.6–3 MPa dissociative adsorption of (C₆H₅)₃As and hydrogenation to benzene were fast at low surface coverage [4]. Therefore, in this study the dissociation of arsenic compounds on the NiMoS surface are also investigated.

Table 2 shows different surface configurations with AsH₃ dissociation (structure **2a–2f**). The dissociation of AsH₃ on the Ni(1 0 0)Mo-edge surface can form adsorbed As atoms on Ni sites and gas-phase H₂ molecules and the process is slightly exothermic as shown by the value of ΔE_{dis} in Table 2. Arsenic atoms prefer the bridge positions between two nickel sites when they initially adsorb on separated nickel sites (structure **2a–2c**). The dissociation energy is −0.34 eV/As for one AsH₃ dissociating on the surface and is reduced slightly to −0.28 eV/As for three AsH₃ dissociating on the surface. Structure **2d** shows the optimized configuration when two arsenic atoms occupied two neighboring nickel sites after dissociation; arsenic atoms are nearly atop of the nickel sites instead of being in the bridge positions between two nickel sites and the dissociation energy is −0.40 eV/As. Almost no repulsion effect was observed, however, when there are more than two arsenic atoms on the surface (structure **2e**). When there are six AsH₃ dissociating on the surface, the arsenic atoms can also go to the bridge positions between nickel sites as shown in structure **2f** and the dissociation energy is also −0.40 eV/As.

The dissociation energies (ΔE_{dis}) for different organoarsenic compounds on the Ni(1 0 0)Mo-edge surface to form structure **2a** are listed in Table 3. The dissociation of the other three organoarsenic molecules on the Ni(1 0 0)Mo-edge (1 0 $\bar{1}$ 0) surface are more exothermic than AsH₃. The energy change (ΔE_{d}^*) for a chemically adsorbed arsenic molecule to dissociate on the Ni(1 0 0)Mo-edge surface to form structure **2a** are also calculated and the values are shown in Table 3. For these four arsenic compounds, however, this process is endothermic, which indicates that

Table 3

Dissociation energy (ΔE_{dis} , calculated by Eq. (2)) of different arsenic compounds and the energy change (ΔE_{dis}^*) for a chemically adsorbed arsenic molecule on the Ni(100)Mo-edge surface (as shown by structures listed in Table 1) to dissociate to form structure 2a. The formulas in parentheses indicate the compounds produced by dissociation. The process is shown with the dissociation of AsH_3 as an example.

Compounds	AsH_3	$(\text{CH}_3)_3\text{As}$	$(\text{C}_2\text{H}_5)_3\text{As}$	$(\text{C}_6\text{H}_5)_3\text{As}$
	−0.34 (H_2)	−1.93 (CH_4)	−1.78 (C_2H_6)	−0.87 (C_6H_6 , benzene)
	+1.36 (H_2)	+0.34 (CH_4)	+0.63 (C_2H_6)	+1.24 (C_6H_6 , benzene)

after the organoarsenic molecules have adsorbed on the catalyst surface, their dissociation on the Ni(100)Mo-edge surface is not energetically favored.

3.2.3. Arsenic substitution

Another possibility for the incorporation of arsenic into NiMoS is to substitute Ni or S atoms on the edge surfaces and the results are shown in Table 4. The energy change for one nickel on the Ni(100)Mo-edge surface being substituted by a As atom (structure

4a) from AsH_3 is −1.77 and −0.71 eV/As when using NiAs and Ni_3S_2 as energy references, respectively. When three Ni atoms are substituted by As atoms (structure 4b), the energy change is slightly reduced to −1.71 and −0.66 eV/As, respectively. According to previous DFT results, the Ni(100)Mo-edge without any sulfur coverage is the most stable structure at typical hydrotreating reaction conditions [13]. Therefore, it is only possible for arsenic to substitute the S atoms on the edge of the basal plane. The energy change ($\Delta E_{\text{sub,S}}$) for one sulfur atom on the basal plane being substituted by one As atom (structure 4c) is 0.65 eV/As.

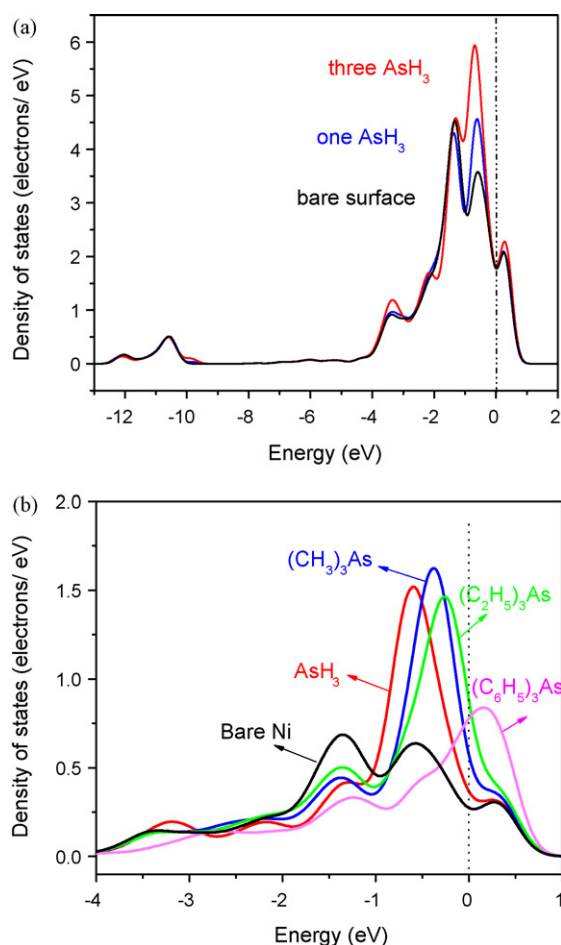


Fig. 3. Local projected density of *d*-states (PDOS) on nickel sites of the bare Ni edge surface and surfaces with one and three adsorbed AsH_3 molecules (a) and the local projected density of *d*-states (PDOS) on a single nickel site of the bare Ni(100)Mo-edge surface and surfaces with indicated arsenic molecules adsorbed on the nickel site.

3.2.4. Incorporation of arsenic into the Ni(50)Mo-edge (10 $\bar{1}$ 0) surface

Additional STM and DFT results by different groups show that there can be partial substitution of Mo by Ni on the Mo-edge [8,13,31]. Therefore, the incorporation of arsenic compounds on a partially promoted Mo-edge surface was also investigated. Substituting one of every two molybdenum atoms on the (10 $\bar{1}$ 0) metal-edge of MoS_2 by nickel atoms generates a partially promoted edge surface, termed the Ni(50)Mo-edge. The most stable structure on the Ni(50)Mo-edge is with one sulfur atom directly atop of each molybdenum atom and nickel atoms being uncovered, as shown in structure 3a of Table 3 in Ref. [8]. The adsorption of AsH_3 ($\Delta E = -1.08$ eV/As), $(\text{CH}_3)_3\text{As}$ ($\Delta E = -1.02$ eV/As), $\text{C}_2\text{H}_5)_3\text{As}$ ($\Delta E = -1.06$ eV/As) and $(\text{C}_6\text{H}_5)_3\text{As}$ ($\Delta E = -0.71$ eV/As) are also energetically favored on the Ni(50)Mo-edge surface, but the adsorption energy is about 1 eV lower than those on the Ni(100)Mo-edge surface, which may be caused by the repulsion effect of the S atoms atop of molybdenum atoms. Arsenic can also incorporate into Ni(50)Mo-edge surface by substituting Ni atoms. The energy change is −1.90 and −1.52 eV/As for one and three nickel being

Table 4

Surface configurations and relative energies (calculated by Eqs. (3) and (4)) for the substitution of Ni (4a and 4b) and S (4c) by arsenic atoms on the Ni(100)Mo-edge surface.

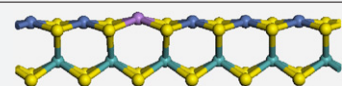
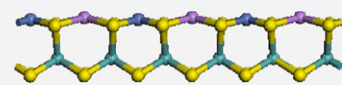
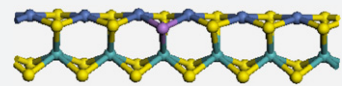
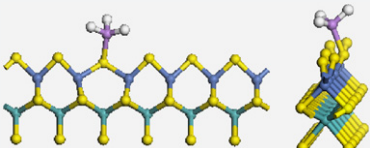
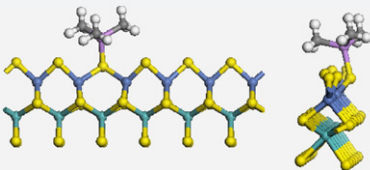
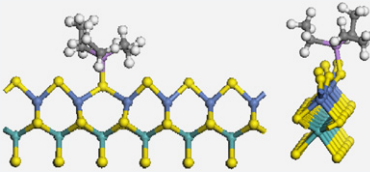
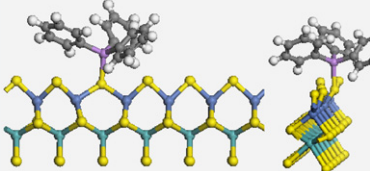
Configurations	Optimized structure	ΔE_{sub} (eV/As)
4a		−1.77
4b		−1.71
4c		0.65

Table 5
Surface configurations of organoarsenic adsorption on the Ni(100)S-edge surface after optimization and the relative energies of optimized configurations with the clean surface and gas-phase molecule as the energetic references.

Configurations	Arsenic compounds	Optimized structure	ΔE_{ads} (eV/As)
5a	AsH ₃		−0.41
5b	(CH ₃) ₃ As		−1.48
5c	(C ₂ H ₅) ₃ As		−1.65
5d	(C ₆ H ₅) ₃ As		−1.25

substituted by arsenic from arsine, respectively. Arsenic cannot incorporate into Ni(50)Mo-edge surface by substituting S atoms atop of molybdenum atoms. The dissociation of arsine is not energetically favored (slightly endothermic) on the Ni(50)Mo-edge surface.

3.3. Incorporation of arsenic into the Ni(100)S-edge ($\bar{1}010$) surface

Substitution of all molybdenum atoms on the MoS₂ ($\bar{1}010$) edge (sulfur-edge) surface by nickel atoms produces the Ni(100)S-edge. Previous DFT and STM studies have shown that the Ni(100)S-edge surface with 50% S coverage (as shown in Fig. 1b) is stable at typical hydrotreating reaction conditions [13,31].

3.3.1. Adsorption of organoarsenic compounds

The adsorption of AsH₃, (CH₃)₃As, (C₂H₅)₃As and (C₆H₅)₃As on the Ni(100)S-edge surface are summarized in Table 5. Calculation results show that the adsorption of arsenic compounds occurred only on the S sites of the Ni(100)S-edge surface. The adsorption energies of these four model arsenic compounds on the Ni(100)S-edge surface of NiMoS catalyst are lower than that on the Ni(100)Mo-edge surface, but still have a high negative value. Similar to that on the Ni(100)Mo-edge surface, the adsorption energies of arsenic compounds on the Ni(100)S-edge surface vary with the different As ligands and also increases in the order of AsH₃ < (CH₃)₃As < (C₂H₅)₃As, but with (C₆H₅)₃As having a lower adsorption energy than that of (CH₃)₃As and (C₂H₅)₃As. Fig. 4 shows that there is also a good correlation between the adsorption energies and the eigenvalues of the HOMOs of the arsenic compounds. The absolute value of the adsorption energy increases with the increase of the HOMO eigenvalues. Fig. 5 shows the local projected density of *p*-states on a single S site of the Ni(100)S-edge

surface and surfaces with indicated arsenic molecules adsorbed on top of this S site. The adsorption of all these four arsenic molecules increased the density of occupied *p*-states of the S site below the Fermi level. These results indicate that the adsorption of arsenic compounds on the Ni(100)S-edge is also stabilized by electron donation from arsenic to the S site of the catalyst surface.

3.3.2. Dissociation of organoarsenic compounds

The dissociation of arsenic compounds on the Ni(100)S-edge surface are also investigated. Different configurations for the dissociation of AsH₃ are listed in Table 6. AsH₃ can dissociate to form As atoms attached on the Ni(100)S-edge surface and gas-phase

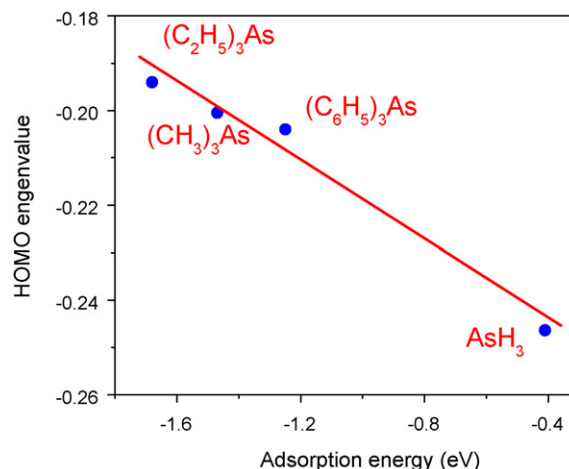


Fig. 4. Correlation between the adsorption energies on Ni(100)S-edge surface and the eigenvalues (in Hartrees) of the HOMO of arsenic compounds.

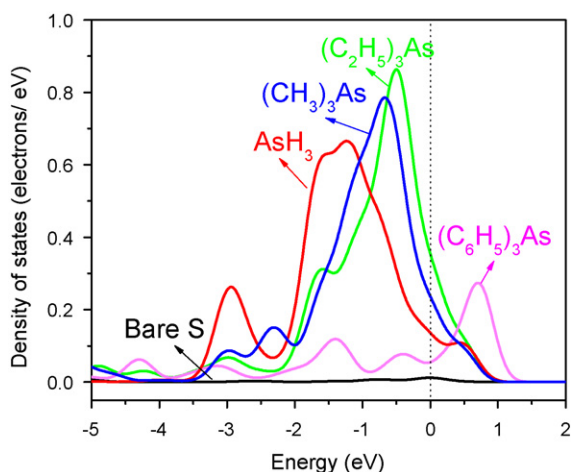


Fig. 5. Local projected density of *p*-states (PDOS) on a single S site of the 50% S covered S edge and on the S atoms with indicated arsenic molecules adsorbed.

Table 6

Surface configurations and relative energies of AsH₃ dissociation on the Ni(1 0 0)S-edge surface. The value of ΔE_{dis} was calculated by Eq. (2).

Configurations	Optimized structure	ΔE_{dis} (eV/As)
6a		0.36
6b		−0.66
6c		−1.22

H₂ molecules. According to the values of ΔE_{dis} , the dissociation of AsH₃ to form the configurations with either an arsenic atom bridging two sulfur atoms (structure **6b**) or two nickel (structure **6c**) atoms is exothermic.

The dissociation energies, ΔE_{dis} , of different arsenic compounds to form structure **6b** are listed in Table 7. The ΔE_{dis} of all these arsenic compounds on the Ni(1 0 0)S-edge surface has a larger negative value than that on the Ni(1 0 0)Mo-edge surface. The energy changes, ΔE_{dis}^* , for the structures with arsenic molecules adsorbed on Ni(1 0 0)S-edge surface to form structure **6b** are also calculated. Different from that on the Ni(1 0 0)Mo-edge surface, the ΔE_{dis}^* of all these arsenic compounds have negative or just slightly positive (for the dissociation of adsorbed (C₆H₅)₃As) values. This indicates that after the arsenic compounds have adsorbed on the Ni(1 0 0)S-edge surface, their subsequent dissociation on this surface is also energetically favored.

3.3.3. Arsenic substitution

Arsenic may also incorporate into Ni(1 0 0)S-edge surface by substituting Ni or S atoms. Different configurations for the substitution are listed in Table 8. The energy change for one nickel atom being substituted by one As atom (structure **8a**) from AsH₃ is −2.44 and −1.45 eV/As with NiAs and Ni₃S₂ as the energy refer-

ences, respectively. The process for one S atom being substituted by As (structure **8b**) is athermic, which is different from that on the Ni(1 0 0)Mo-edge surface. This may due to the weaker bonding between the terminal sulfur atoms and the Ni atoms on the Ni-promoted (1 0 1 0) edge [19].

3.4. Comparison of arsenic incorporation into the two edge surfaces

By comparing the incorporation of arsenic into Ni fully promoted Mo- and S-edge surface of NiMoS, it was found that for the simple adsorption of organoarsenic compounds on the edge surfaces the adsorption on the Ni(1 0 0)Mo-edge surface is energetically more favorable than on the Ni(1 0 0)S-edge surface. However, after the arsenic molecules have adsorbed on the edge surface, their dissociation on a Ni(1 0 0)S-edge surface is energetically favorable. Arsenic may substitute Ni atoms on both Ni(1 0 0)Mo-edge and Ni(1 0 0)S-edge surfaces. The substitution of S atoms by arsenic, however, may only occur on a Ni(1 0 0)S-edge surface based on the calculated energetics.

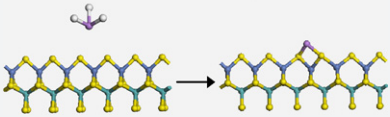
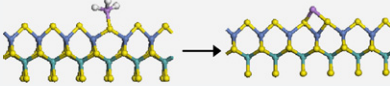
4. Comparison with previous results

4.1. Comparison with the absorption of H₂, sulfur- and nitrogen-containing molecules on NiMoS

During the hydrotreatment of oil fractions, organic sulfur and nitrogen compounds are adsorbed and activated on the catalyst surfaces. Mutual inhibitory effects between different groups of compounds due to the competitive adsorption on the active sites of catalyst have been observed. In previous studies by Sun et al., the adsorption of H₂, H₂S [8,34], and various nitrogen containing compounds [24,25] and the adsorption thermodynamic data of H₂, H₂S, NH₃, thiophene, pyridine, pyrrole and aniline on the Ni(1 0 0)Mo-edge surface of NiMoS [35] have been investigated using DFT. The results have shown that basic nitrogen molecules have the strongest adsorption energies and thus would show stronger inhibition than other compounds. Compared with the adsorption of basic nitrogen compounds, arsenic compounds have a much higher adsorption energy on the Ni(1 0 0)Mo-edge surface (the adsorption of pyridine and quinoline is −1.29 and −1.14 eV/N, respectively). The free energy changes (ΔG) for the adsorption of arsenic compounds on the Ni(1 0 0)Mo-edge surface are calculated by Eq. (5). The ΔG values as a function of arsenic compounds concentration under a typical hydrotreating condition (temperature of 650 K and a hydrogen pressure of 5.0 MPa) are shown in Fig. 6. The negative values of ΔG increase with increasing arsenic concentrations in the reactant. At a certain arsenic concentrations, the negative values of ΔG increase in the order of AsH₃ < (CH₃)₃As < (C₂H₅)₃As < (C₆H₅)₃As, and keep a very high negative value even at a very low arsenic concentration, where $P_{\text{As}/\text{H}_2} = 10^{-4}$ ppb, e.g. the partial pressure of arsenic compound in the reactant feed is 5.0×10^{-7} Pa.

The adsorption of H₂, and sulfur- and nitrogen-containing molecules on the Ni(1 0 0)S-edge surface of NiMoS has been scarcely studied. Nevertheless, the current calculation results have shown that the adsorption of organoarsenic compounds on the Ni(1 0 0)S-edge surface are also very strong although their adsorption energies on the Ni(1 0 0)S-edge surface are slightly lower than those on the Ni(1 0 0)Mo-edge surface. These results indicate that arsenic compounds have very strong interaction energetics with the NiMoS catalyst surface such that they are very difficult to remove from the NiMoS catalyst surface once adsorbed. Therefore, although the concentrations of organoarsenic compounds in crude oils are only in low ppm or ppb levels, arsenic deactivation of NiMoS

Table 7
Dissociation energy (ΔE_{dis} , calculated by Eq. (2)) of different arsenic compounds and the energy change (ΔE_{dis}^*) for a chemically adsorbed arsenic molecule on the Ni(1 0 0)S-edge surface (as shown by structures listed in Table 5) to dissociate to form structure **6b**. The formulas in parentheses indicate the compounds produced by dissociation. The process is shown with the dissociation of AsH₃ as an example.

Compounds	AsH ₃	(CH ₃) ₃ As	(C ₂ H ₅) ₃ As	(C ₆ H ₅) ₃ As
ΔE_{dis} (ev/As)				
	−0.66 (H ₂)	−2.24 (CH ₄)	−2.10 (C ₂ H ₆)	−1.19 (C ₆ H ₆ , benzene)
ΔE_{dis}^* (ev/As)				
	−0.25 (H ₂)	−0.76 (CH ₄)	−0.45 (C ₂ H ₆)	0.06 (C ₆ H ₆ , benzene)

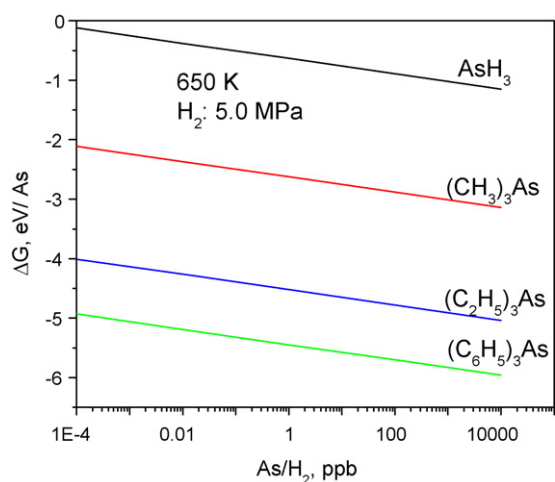


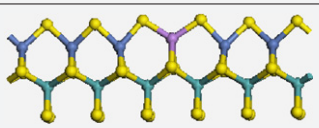
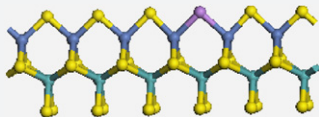
Fig. 6. The free energy changes of arsenic compounds adsorption process as a function of arsenic concentration at 650 K and a hydrogen pressure of 5.0 MPa.

hydrotreating catalysts will still be severe.

4.2. Comparison with X-ray absorption results

The chemical state of arsenic deposited on a NiMoP/Al₂O₃ hydrotreating catalyst exposed to ppb levels of arsenic over several years in a refinery reactor has been previously studied by EXAFS [7]. In the as-received As-NiMoP catalyst, arsenic is exclusively coordinated to oxygen atoms. Upon sulfiding the sample in a gas mixture of 2% H₂S/2% H₂/96% He, the As atoms become sur-

Table 8
Surface configurations and relative energies for the substitution of Ni (**8a**) and S (**8b**) by an arsenic atom on the Ni(1 0 0)S-edge surface. The value of ΔE_{sub} was calculated by Eqs. (3) and (4).

Configurations	Optimized structure	ΔE_{sub} (eV/As)
8a		−2.44
8b		0

rounded by approximately two sulfur atoms ($N_{\text{As-S}} = 1.8 \pm 0.5 \text{ \AA}$ and $d_{\text{As-S}} = 2.22 \pm 0.02 \text{ \AA}$) according to the EXAFS measurements. Based on the combined EXAFS results, STM data and FEFF8.0 simulations, a possible model (as shown in Fig. 4 of Ref. [7]) for the local environment of As was suggested by the authors. In this model, Ni fully substituted Mo atoms on the (1 0 1 0)S-edges of a hexagonally truncated Ni–MoS₂ slab; an As atom is located at one of the Ni–Mo–S (1 0 1 0) S-edge and is blocking the active NiMoS site by bridging two terminal sulfur atoms. No evidence was found from EXAFS experiments for the formation of a Ni–As bond. It should be noted here that the catalyst was re-sulfided before the EXAFS experiment and the re-sulfidation might change the surface structure of the catalyst and therefore change the chemical state of arsenic in the catalyst. An *in situ* EXAFS experiment on an arsenic poisoned NiMoS catalyst is essential to reveal the chemical state of arsenic, which will provide fundamental information on the mechanism of arsenic deactivation.

In the current DFT study, the incorporation of arsenic into both Ni promoted (1 0 1 0) metal- and (1 0 1 0) S-edges was investigated. It was found that for the simple adsorption of arsenic compounds on the edge surface, the adsorption on Ni(1 0 0)Mo-edge surface is energetically more favorable than on the Ni(1 0 0)S-edge surface. After the arsenic molecules have adsorbed on the edge surfaces, however, their dissociation on a Ni(1 0 0)S-edge surface is much easier, which indicates that organoarsenic molecules prefer to react on the Ni(1 0 0)S-edge if both Ni(1 0 0)Mo-edge and Ni(1 0 0)S-edge exist in the NiMoS catalyst. Moreover, one of the configurations with arsenic atom on the Ni(1 0 0)S-edge surface (structure **6b**) obtained by DFT is consistent with the model suggested in the above mentioned EXAFS study [7]. In structure **6b**, the As atom is coordinated by two sulfur atoms and the As–S distance is 2.25 Å, which is very close to the experiment value ($d_{\text{As-S}} = 2.22 \pm 0.02 \text{ \AA}$).

5. Conclusions

The energetics for the incorporation of arsenic into NiMoS hydrotreating catalysts were studied by DFT calculations using model organoarsenic compounds, AsH₃, (CH₃)₃As, (C₂H₅)₃As, and (C₆H₅)₃As. The adsorption of these organoarsenic compounds are energetically favored on both fully promoted Ni(1 0 0)Mo-edge and Ni(1 0 0)S-edge surfaces and the adsorption takes place through electronic donation from organoarsenic molecules to the catalyst surface. The highly negative adsorption energies indicate the strong adsorption strength of organoarsenic compounds on NiMoS catalyst surfaces. Compared with the adsorption of basic nitrogen compounds, arsenic compounds have a much higher adsorption energy on the Ni(1 0 0)Mo-edge surface. Calculation results on the

dissociation of organoarsenic compounds on the NiMoS surfaces show that adsorption on Ni(100)S-edge surfaces facilitates dissociation of all the molecules investigated. The chemical state of arsenic in one of the calculated configurations, in which the arsenic atom is located at the Ni–Mo–S ($\bar{1}010$) S edge and blocks the active NiMoS site by bridging two terminal sulfur atoms, is consistent with that obtained from previously reported EXAFS experiments. Arsenic may also incorporate into NiMoS catalyst by substituting Ni or S atoms on the edge surfaces. The substitution of Ni atoms by arsenic may occur on both Ni(100)Mo-edge and Ni(100)S-edge surfaces. Substitution of S atoms by arsenic, however, may only occur on the Ni(100)S-edge surface. Experimental investigations on the mechanism of arsenic incorporation and the effect of arsenic incorporation into NiMoS catalyst on the adsorption of H_2 , H_2S and organosulfur and organonitrogen compounds will be the focus of future studies.

Acknowledgements

Financial support for this work was provided by Syncrude Canada Ltd and the Natural Sciences and Engineering Research Council (NSERC) of Canada.

References

- [1] P. Sarrazin, C.J. Cameron, Y. Barthel, M.E. Morrison, *Oil Gas J.* 91 (1993) 86.
- [2] O.K. Bhan, Arsenic removal catalyst and process for making same, United States Patent 6,759,364 (2004).
- [3] J.B. Stigter, H.P.M. de Haan, R. Guicherit, C.P.A. Dekkers, M.L. Daane, *Environ. Pollut.* 107 (2000) 451.
- [4] Y.A. Ryndin, J.P. Candy, B. Didillon, L. Savary, J.M. Basset, *J. Catal.* 198 (2001) 103.
- [5] V. Maurice, Y.A. Ryndin, G. Bergeret, L. Savary, J.P. Candy, J.M. Basset, *J. Catal.* 204 (2001) 192.
- [6] B. Nielsen, J. Villadsen, *Appl. Catal.* 11 (1984) 123.
- [7] A. Puig-Molina, L.P. Nielsen, A.M. Molenbroek, K. Herbst, *Catal. Lett.* 92 (2004) 29.
- [8] M. Sun, J. Adjaye, A.E. Nelson, *Catal. Today* 105 (2005) 36.
- [9] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, *J. Catal.* 187 (1999) 109.
- [10] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, *J. Catal.* 189 (2000) 129.
- [11] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, *J. Catal.* 190 (2000) 128.
- [12] H. Schweiger, P. Raybaud, H. Toulhoat, *J. Catal.* 212 (2002) 33.
- [13] M. Sun, A.E. Nelson, J. Adjaye, *J. Catal.* 226 (2004) 32.
- [14] P. Faye, E. Payen, D. Bougeard, *J. Mol. Model.* 5 (1999) 63.
- [15] L.S. Byskov, M. Bollinger, J.K. Nørskov, B.S. Clausen, H. Topsøe, *J. Mol. Catal. A* 163 (2000) 117.
- [16] V. Alexiev, R. Prins, Th. Weber, *Phys. Chem. Chem. Phys.* 3 (2001) 5326.
- [17] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, *J. Phys. Chem. B* 104 (2000) 11220.
- [18] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, *J. Phys. Chem. B* 106 (2002) 5659.
- [19] A. Traver, H. Nakamura, R.A. van Santen, S. Cristol, J.F.E. Payen, *J. Am. Chem. Soc.* 124 (2002) 7084.
- [20] P. Raybaud, J. Hafner, G. Kresse, H. Toulhoat, *Phys. Rev. Lett.* 80 (1998) 1481.
- [21] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, J. Hafner, F. Hutschka, *Stud. Surf. Sci. Catal.* 127 (1999) 327.
- [22] H. Yang, C. Fairbridge, Z. Ring, *Energy Fuels* 17 (2003) 387.
- [23] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, F. Hutschka, S. Clémendot, *J. Catal.* 224 (2004) 138.
- [24] M. Sun, A.E. Nelson, J. Adjaye, *J. Catal.* 231 (2005) 223.
- [25] M. Sun, A.E. Nelson, J. Adjaye, *Catal. Today* 109 (2005) 49.
- [26] A.D.J. Becke, *Chem. Phys.* 88 (1988) 2547.
- [27] J.P. Perdew, Y. Wang, *Phys. Rev. B* 45 (1992) 13244.
- [28] M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* 86 (1987) 866.
- [29] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* 80 (1993) 1431.
- [30] J.V. Lauritsen, S. Helveg, E. Lægsgaard, I. Stensgaard, B.S. Clausen, H. Topsøe, F. Besenbacher, *J. Catal.* 197 (2001) 1.
- [31] J.V. Lauritsen, J. Kibsgaard, G.H. Olesen, P.G. Moses, B. Hinnemann, S. Helveg, J.K. Nørskov, B.S. Clausen, H. Topsøe, E. Lægsgaard, F. Besenbacher, *J. Catal.* 249 (2007) 220.
- [32] A. Traver, C. Dujardin, F. Mauge, E. Veilly, S. Cristol, J.F. Paul, E. Payen, *J. Phys. Chem. B* 110 (2006) 1261.
- [33] C.F. Ng, H. Ye, L. She, H. Chen, S.Y. Lai, *Appl. Catal. A: Gen.* 171 (1998) 293.
- [34] M. Sun, A.E. Nelson, J. Adjaye, *J. Catal.* 233 (2005) 411.
- [35] M. Sun, A.E. Nelson, J. Adjaye, *Catal. Lett.* 109 (2006) 133.