

Density-functional theory (DFT) modeling of arsenic deactivation of NiMoS using representative organoarsenic compounds

Shaofeng Yang¹, John Adjaye², and Alan E. Nelson^{1*}

¹University of Alberta, Edmonton, Alberta T6G 2G6 (Canada)

²Edmonton Research Centre, Syncrude Canada Ltd, Edmonton, Alberta T6N 1H4 (Canada)

* alan.nelson@ualberta.ca

Introduction

The presence of arsenic as arsine and organoarsenic compounds in petroleum has been recognized to have a dramatic influence on catalyst activity [1]. Several recent studies have demonstrated that on a Ni/Al₂O₃ catalyst, arsenic deactivation proceeds via a stepwise process to form crystalline NiAs [2]. Additionally, studies using nickel reforming catalysts have also discussed the formation of Ni₅As₂ and NiAs nickel alloy phases [3]. However, there is a paucity of information regarding the mechanism and chemical state of arsenic after deposition on a NiMoS hydrotreating (HYT) catalyst. Considering the low amount of nickel in NiMoS HYT catalysts and the unique structure of the bimetallic NiMoS phase, the deactivation mechanism of NiMoS is expected to be different than the mechanism for highly loaded Ni-Al₂O₃ catalysts. Thus, the need to clarify these issues and understand the deactivation mechanism and energetics of NiMoS by arsenic is of fundamental importance for the HYT of arsenic containing petroleum. In this research, molecular simulation (density-functional theory) is utilized to develop a comprehensive understanding of these issues.

Materials and Methods

The NiMoS periodic catalyst model has been used previously to study the adsorption of heavy organonitrogen compounds [4]. The model is repeated in the x-direction with a periodicity of six MoS₂ units with Mo atoms on the edge surface substituted by Ni atoms to form a fully nickel promoted surface (the Ni-edge surface). The energy calculations are based on density-functional theory (DFT), and have been performed using Materials Studio DMol³ from Accelrys (ver. 3.2). The DNP basis sets and GGA-PW91 exchange correlation functions 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 are used to treat core electrons of molybdenum, nickel and arsenic.

Results and Discussion

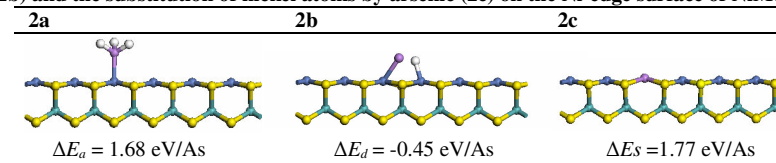
The adsorption of AsH₃, (CH₃)₃As, (C₂H₅)₃As and (C₆H₅)₃As, on a fully nickel promoted surface is energetically favored (Table 1). The highly negative ΔE_a values indicate the strong adsorption strength of organoarsenic compounds on NiMoS. When more arsenic molecules are adsorbed on the surface, the adsorption energy is reduced because of a repulsion effect. The adsorption of arsenic molecules can not occur on the S sites on the surface; when they are initially put on top of S atoms, they moved to on top of Ni atoms after geometry optimization. The adsorption energies of arsenic compounds vary with the different ligands of arsenic (constituents of H in AsH₃). There is correlation between the adsorptivity of the arsenic compounds with their electronic structures, specifically the Mulliken atomic charges and the eigenvalues of the highest occupied molecular orbital (HOMO). The adsorption energy of arsenic compounds is much higher than that of the N-containing compounds, such as pyridine

($\Delta E_a = -1.29$ eV/N) [4] and quinoline ($\Delta E_a = -0.92$ eV/N) [5]. The free energy changes of the adsorption process are highly negative even at very low arsenic concentrations (partial pressure of As 5.0×10^{-7} Pa). Additionally, adsorbed arsenic molecules can dissociate on the Ni-edge surface. One AsH₃ can dissociate to form a pair of Ni-As and Ni-H (structure 2b) or S-H and a gas phase H₂. Arsenic atoms prefer the bridge positions between two nickel sites. Arsenic can also incorporate into NiMoS by substituting Ni atoms (structure 2c) accompanied by the formation of NiAs, which is energetically favored compared to simple adsorption on the Ni-edge surface. The energy change for all the six Ni atoms on the Ni-edge surface being substituted by arsenic atoms (with AsH₃ as reference) is -1.68 eV/As.

Table 1. Adsorption energies (ΔE_a) of arsenic compounds on a fully nickel promoted surface and Mulliken atomic charges of As and HOMO eigenvalues of the arsenic compounds

Compounds	AsH ₃	(CH ₃) ₃ As	(C ₂ H ₅) ₃ As	(C ₆ H ₅) ₃ As
ΔE_a (eV/As)	-1.68	-2.27	-2.41	-2.11
Mulliken charge	-0.158	-0.004	0.054	0.151
HOMO eigenvalues	-0.2464	-0.2005	-0.1940	-0.2025

Table 2. Surface configurations and relative energies of arsine adsorption (2a), dissociation (2b) and the substitution of nickel atoms by arsenic (2c) on the Ni-edge surface of NiMoS



The incorporation (both adsorption and substitution) of arsenic into NiMoS can inhibit the adsorption of molecular H₂ and H₂S on both the fully promoted Ni-edge and Ni(50)Mo-edge surfaces. Organoarsenic adsorption reduces the adsorption energy of molecular H₂ and H₂S on nickel sites. On a surface with nickel atoms being substituted by arsenic, the arsenic sites are not active for the chemical adsorption of any hydrogen species.

Significance

The mechanism and energetics of arsenic deposition on NiMoS is studied using DFT to provide the fundamental insight into the deactivation of hydrotreating catalyst used for arsenic containing streams.

References

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