

# Periodic DFT Investigation on the Adsorption and Catalytic Desulfurization of Thiophene over VC(001) and VN(001) via Hydrogenation and Direct Pathways.

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## Introduction

The imposition of stringent environmental restrictions on the S-content of petroleum derivatives makes necessary efforts in the development of new catalysts<sup>1</sup>. Particularly, vanadium nitrides and carbides are active in desulfurization reactions<sup>2</sup>. However, experimental and theoretical studies on the surface properties and reaction mechanisms are quite scarce. In this work, we carried out a detailed computational investigation on the aspects involved in thiophene adsorption and desulfurization processes over VC(001) and VN(001) surfaces. The effects of thiophene hydrogenation were also studied and possible mechanisms involved in bond breaking were discussed.

Total-energy calculations were performed using the PWSCF computational code<sup>3</sup>. The Kohn-Sham states were expanded in plane-waves up to a kinetic energy cutoff of 30 Ry. The PBE functional was used to calculate the exchange and correlation contributions. Integrals over the Brillouin-zone were performed by sums of 2x2x1 Monkhorst-Pack. The slab was divided into four atomic layers and a vacuum region of ~15 Å was applied. The NEB method<sup>4</sup> was used in order to locate energy barriers and transitions states through the minimum energy path.

## Results and Discussion

Our theoretical calculations suggest that on VC(001) thiophene molecules adsorb preferentially in a partially-tilted  $\eta^1$  configuration with the ring S atom forming a covalent bond with a V(Surf) atom and with small modification in the intramolecular structure. On VN(001) thiophene molecules prefer to interact with the ring orthogonally located on a surface hollow site. The calculated energies indicated that adsorption on both surfaces (Fig. 1) are exothermic and that the catalytic activity are related to surface effects (corrugation and reconstruction). Our calculations confirm that the

surfaces present resistance to sulfur deposition and the analysis of the electronic properties confirms the participation of the non-metal surface atoms in the adsorption.

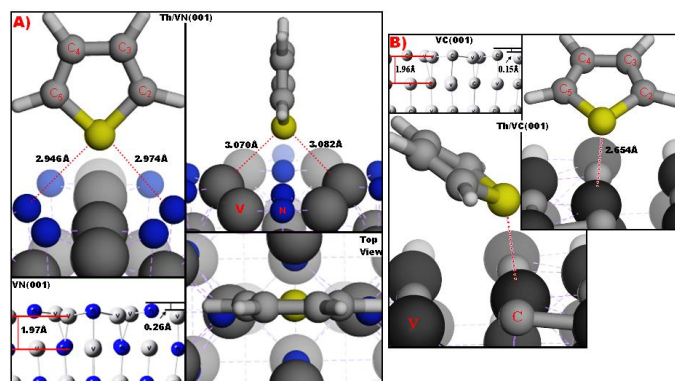


Fig 1 - Configurations of the most stable (Th@VN(001) (A) and the Th@VC(001) (B) adsorption systems.

Our calculations indicate that the removal of sulfur starts with the S-C<sup>2</sup> scission, followed by the cleavage of the S-C<sup>5</sup> bond.

## Conclusions

The present work indicates that the HYD pathway is more difficult to achieve for the S-C cleavage process. For both surfaces, the substantial increase of the energy barriers caused by ring hydrogenation reveals a preference for the DDS pathway instead of HYD in qualitative resemblance to noble metal surfaces<sup>5</sup>.

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